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COLLABORATIVE STUDY OF METHOD FOR THE DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES (PORTLAND CEMENT PLANTS)

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16. ABSTRACT

This report presents and analyzes the results of a collaborative test of EPA Method 5–Determination of Particulate Emissions from Stationary Sources. The test was conducted by four participating laboratories at a Portland cement plant under simulated "real world" Method 5 testing conditions. This report describes the collaborative test, examines problems encountered in the use of Method 5, estimates the between-laboratory and within-laboratory precision of Method 5, ascribes precision variability to its sources, and evaluates the necessity of sampling restrictions required for compliance testing. The magnitude of the Method 5 precision estimates obtained is due primarily to occasional extremely high particulate determinations. This high value phenomenon, present in all three Method 5 collaborative tests that have been conducted by Southwest Research Institute is believed caused by accidental scraping of the probe tip against the stack wall. Hypothetical estimates of Method 5 precision are made with the high values excluded from the data.

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SUMMARY AND CONCLUSIONS

This report presents and analyzes the results of a collaborative test of Method 5–Determination of Particulate Emissions from Stationary Sources. Method 5 was promulgated by the Environmental Protection Agency in the *Federal Register* on December 23, 1971. This method specifies that the particulate concentration is determined from the particulate matter withdrawn isokinetically from the source and determined gravimetrically after removal of uncombined water.

A Portland cement plant utilizing the wet feed process was the collaborative test site. The testing was conducted with minimal supervisory interference to simulate actual "real world" usage of Method 5 as much as possible. The four participating collaborative laboratory teams made a total of 15 simultaneous sampling runs on the stack over a two-week period. Because the cement plant frequently experienced upset conditions during the testing period, the true average particulate emission concentration sampled sometimes varied by a factor of two from one run to the next.

Various problems associated with the use of Method 5 become apparent upon preliminary analysis of the data submitted by the collaborative laboratories. One collaborator's entire set of test data had to be rejected because, due to an internal failure to communicate, the collection and weighing of the particulate samples were done by another method that was inconsistent with Method 5. Numerous minor calculation errors are contained in the remaining three collaborators' reported results. After the calculation errors are corrected, it is evident that the sampling was often deficient. One collaborator had difficulty achieving an isokinetic sampling rate, presumably because of inaccurate calibration of his dry gas meter. Another collaborator frequently sampled a slightly insufficient gas volume. The preceding problems are more attributable to operator error generally caused by inexperience with Method 5 than to method inadequacy. Another usage problem with more serious consequences for Method 5 is the occasional determination of extremely high particulate concentrations. This high value phenomenon is believed caused by accidental scraping of particulate matter adhering to the stack wall into the sampling probe tip during its insertion or removal through a sampling port. In the dirty (and difficult) sampling environment in which Method 5 must be performed, occasional accidental scraping with its concomitant high particulate determinations is likely to plague Method 5.

The valid corrected Method 5 determinations were given a thorough statistical analysis, including data adjustment as appropriate, to estimate the precision of Method 5 in cement plant applications and to investigate as many of the sources of precision variation as possible. The following conclusions emerge from the statistical analysis:

A. Precision

The estimated precision of a Method 5 particulate concentration determination from a cement plant stack is expressed in terms of the between-laboratory standard deviation and the within-laboratory standard deviation. Since both of these standard deviations are proportional to their respective group means, it is appropriate to utilize the weighted coefficient of variation technique to estimate both standard deviations as a percentage of the "true" Method 5 concentration determination value, δ. Precision estimates for Method 5 in cement plant applications are derived for two relevant situations: Method 5 as actually used by the collaborators, and Method 5 without the high value phenomenon.

(1) **Method 5.** The following precision estimates are obtained from those particulate determinations obtained on the cement plant collaborative test that are valid and acceptable by Method 5:

(a) Between-laboratory. The between-laboratory standard deviation of Method 5 is estimated to be 58.4% of δ. Because there are a maximum of three valid collaborator determinations per run, this estimate has only 2 degrees of freedom.

(b) Within-laboratory. The estimated within-laboratory standard deviation of Method 5 is 28.4% of δ and also has 2 degrees of freedom associated with it.

(2) **Method 5 Exclusive of the High Value Phenomenon.** If the high value phenomenon could be eliminated from Method 5 through suitable modification to the method, much better precision would exist. The following estimates pertain to this hypothetical situation:

(a) Between-laboratory. The estimated between-laboratory standard deviation is 20.1% of δ, with 2 associated degrees of freedom.

(b) Within-laboratory. The within-laboratory standard deviation is estimated with 20 degrees of freedom as 9.8% of δ.

Now the between-laboratory estimates contain only 2 degrees of freedom. So does the Method 5 within-laboratory estimate. The population of laboratories could differ substantially from the three acceptable collaborators in this collaborative test. Thus, the true between-laboratory standard deviations and the true Method 5 within-laboratory standard deviation may differ substantially from their estimated values, perhaps by more than a factor of 2, in either direction. However, the hypothetical version within-laboratory standard deviation estimate, based on 20 degrees of freedom, is reasonably precise.

B. Sources of Precision Variation

The between-laboratory variance estimated for Method 5 from the cement plant collaborative test can be apportioned into its components to indicate those areas in which precision improvements would be profitable. Over 88 percent of the estimated between-laboratory variance is due to the high value phenomenon effect. Of the usual variation sources, laboratory bias factors account for 9%, while the within-laboratory factors cause less than 3%. If the cement plant precision of Method 5 is to be substantially improved, means must be developed to minimize the effects of probe contamination through accidental scraping so that the high value phenomenon can be controlled. Further standardization of Method 5 by specifying more procedural details should reduce the laboratory bias effect.

Method 5 now contains two sampling restrictions: limitation of the percent of isokinetic sampling I to the range $90 \leq I \leq 110$, and a minimum dry gas sampling volume of 60 scf. These restrictions were intended to prevent deterioration of Method 5's precision. The isokinetic restriction $90 \leq I \leq 110$ is essential to maintain the between-laboratory and the within-laboratory precision estimated herein for cement plant applications. However, rigid adherence to the 60 scf minimum sampling volume is unnecessary; acceptance of sampling volumes slightly below 60 scf has no detrimental effect on the estimated Method 5 precision.

Based on the preceding conclusions and on the collaborators' experiences and suggestions, several recommendations are presented for consideration in revising Method 5. The intent of these recommendations is to minimize the high value problem and to further standardize the usage of Method 5, so that its precision will be improved.

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I. INTRODUCTION

This report describes the work performed and the results obtained on Southwest Research Institute Project 01-3462-003, Contract No. 68-02-0626, which includes collaborative testing of Method 5 for particulate emissions as given in "Standard of Performance for New Stationary Sources."[1]*

This report describes the collaborative testing of Method 5 in a Portland cement plant and gives the statistical analysis of the data from the collaborative test and the conclusions and recommendations based on the analysis of data.

*Superscript numbers in parentheses refer to the References at the end of this report.

II. COLLABORATIVE TESTING OF METHOD 5

A. Collaborative Test Site

Arrangements were made for a collaborative test of Method 5 at the Lone Star Industries Portland cement plant in Houston, Texas.

The plant site was visited in February 1972 to evaluate suitability for collaborative testing. The plant utilizes the wet feed process and operates three kilns. The flue gas from each kiln passes through a separate electrostatic precipitator. These flue gases are then combined and fed into a 300-ft-high stack. The clinker cooler is used to preheat the air to the main kilns, so that the clinker cooler outlet does not constitute an emission source. Plant capacity is 1700 tons/day, dry feed basis.

There are four sample ports spaced 90 deg apart, and located 150 ft above grade. The inside stack diameter at the sample ports is 13 ft. The stack is of double-walled construction, with the outer supporting wall of reinforced concrete. The inner stack, separated from the outer stack by an annular space of one foot, is constructed of refractory brick. The sample ports are installed in the inner stack and are accessable through openings in the outer stack wall. The sample ports are located 90 feet (6.9 diameters) above the inlet duct to the stack and 150 feet (11.5 diameters) below the stack outlet. Twenty traverse points were used in the tests, ten per diameter. Permanent monorails were installed by Lone Star Industries at each sample port. Access to the sample ports is provided by a 360-deg platform on the stack. A second 360-deg platform on the stack at 125 ft above grade provided space for the control consoles. The stack is equipped with a bolometer at the 125-ft level, which provides in-stack opacity readings. Arrangements were made to obtain both daily raw material feedrates and in-stack plume opacities during the test period.

An overall view of the stack and sampling platforms is shown in Figure 1. A schematic of the sampling platform and sampling port is given in Figure 2. Typical velocity profiles are shown in Figure 3.

Figure 1. Portland Cement Plant Test Site

B. Collaborators

The collaborators for the Lone Star Industries Portland cement plant test were Mr. Charles Rodriguez and Mr. Nollie Swynnerton of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Mike Taylor and Mr. Ron Hawkins of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Quirino Wong, Mr. Randy Creighton, and Mr. Vito Pacheco, Department of Public Health, City of Houston, Houston, Texas; and Mr. Royce Alford, Mr. Ken Drummond, and Mr Lynn Cochran of Southwestern Laboratories, Austin, Texas.*

Collaborative tests were conducted under the general supervision of Dr. Henry Hamil of Southwest Research Institute. Dr. Hamil had the overall responsibility for assuring that the collaborators were competent to perform the test, that the test was conducted in accordance with the collaborative test plan, and that all collaborators adhered to Method 5 as written in the *Federal Register*, December 23, 1971.

*Throughout the remainder of this report, the collaborative laboratories are referenced by randomly assigned code numbers as Lab 101, Lab 102, Lab 103, and Lab 104. These code numbers do not correspond to the above ordered listing of collaborators.

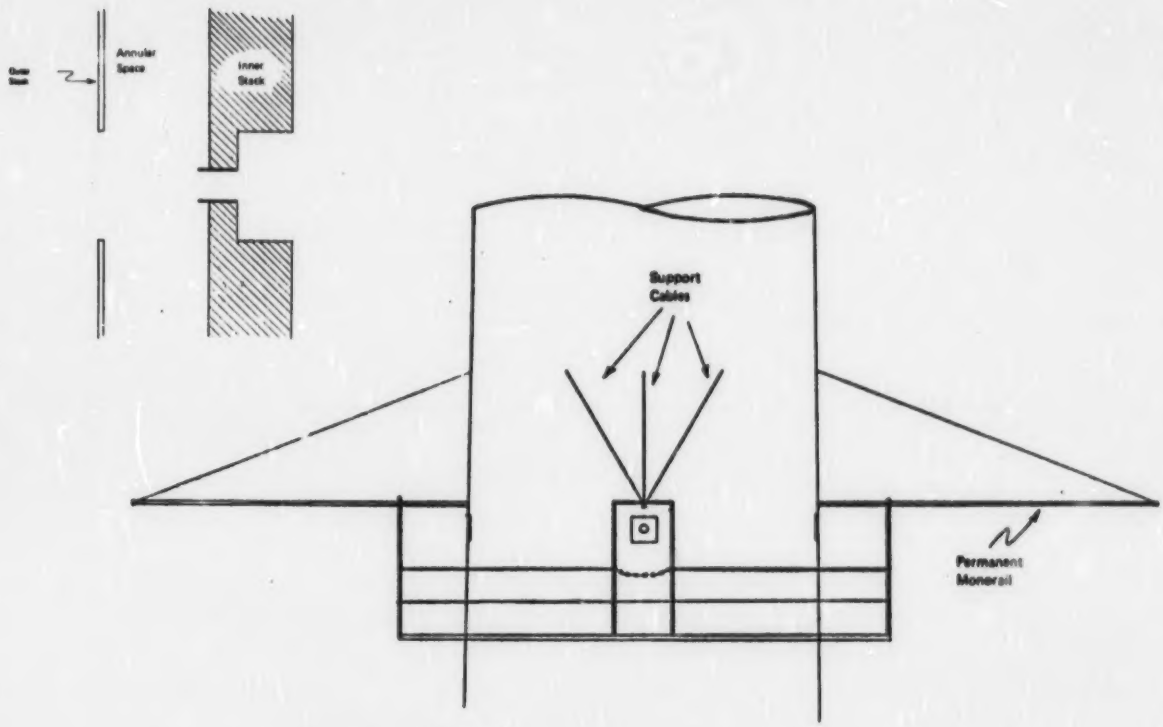


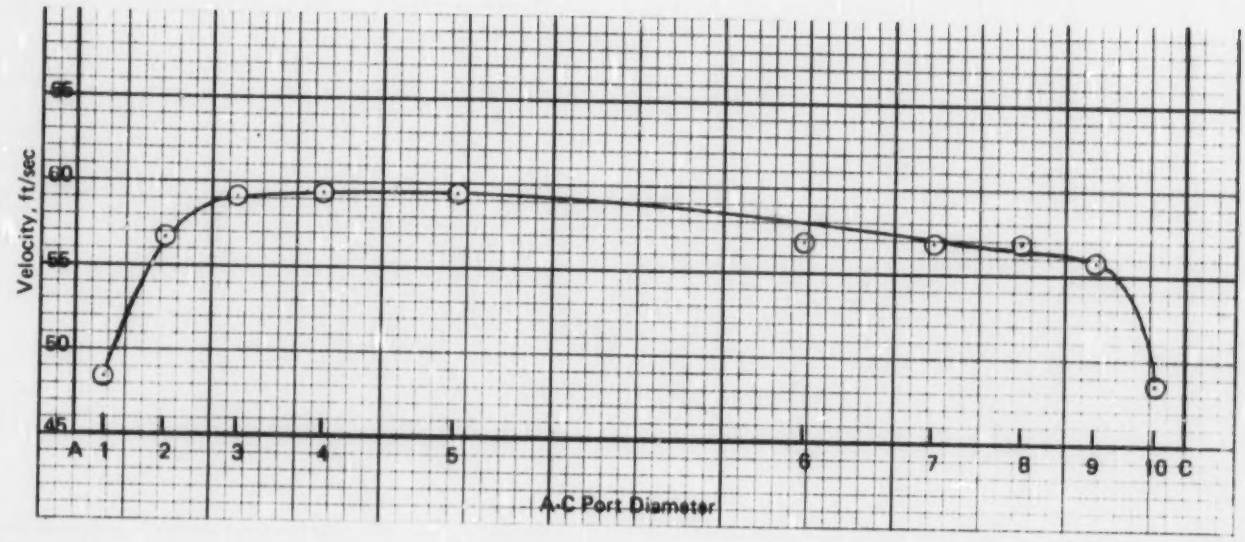
Figure 2. Platform Configuration at Sampling Level

C. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the tests discussed in this report involves conducting the test in such a manner as to simulate "real world" testing as closely as possible. "Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision, and without any additional information from outside sources, i.e., test supervisor or other collaborators.

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. If random experimental errors were observed, such as mismeasurement of volume of impinger solution, improper rinsing of probe, etc., no interference was made by the test supervisor. Since such random errors will occur in the everyday use of this method in the field, unduly restrictive supervision of the collaborative test would bias the method with respect to the performance test results which will be obtained when the method is put into general usage. However, if gross deviations were observed of such magnitude as to make it clear that the collaborator was not following the method as written, these would be pointed out to the collaborator and corrected by the test supervisor.

While most of the instructions in the *Federal Register* are quite explicit, some areas are subject to interpretation. Where this was the case, the individual collaborators were allowed to exercise their professional judgment as to the interpretation of the instructions.



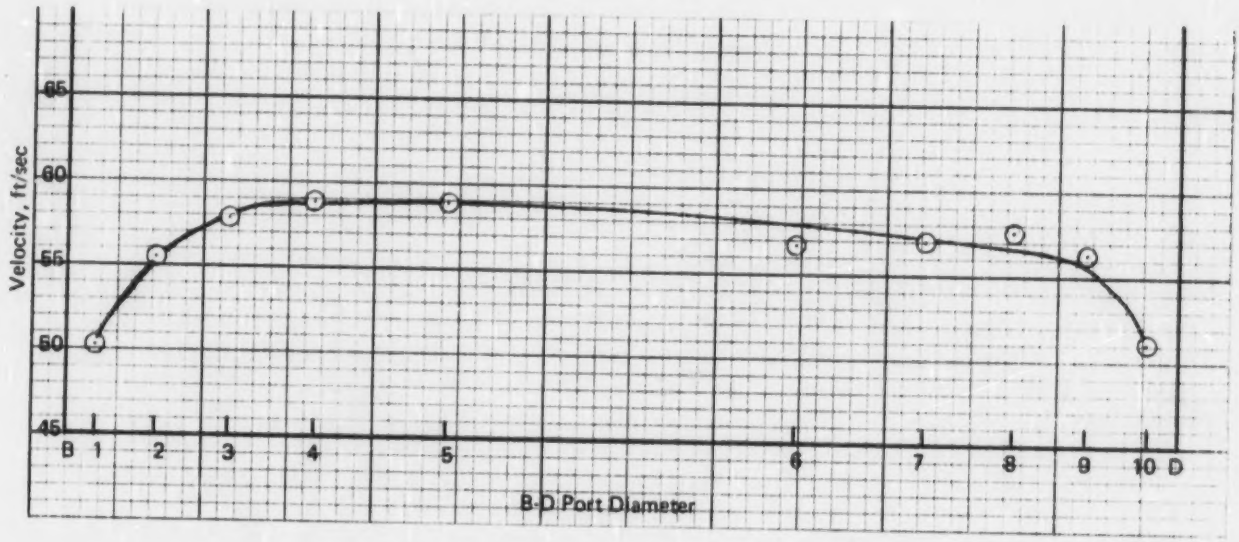


Figure 3. Typical Velocity Profiles
Lone Star Portland Cement Plant

The overall basis for this so-called "real-world" concept of collaborative testing is to evaluate the subject method in such a manner as to reflect the reliability and precision of the method that would be expected in performance testing in the field.

III. STATISTICAL DESIGN AND ANALYSIS

A. Statistical Terminology

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in this report. The procedures for obtaining estimates of the pertinent values are developed and justified in the subsequent sections.

We say that an *estimator*, $\hat{\theta}$, *is unbiased for a parameter* θ if the expected value of $\hat{\theta}$ is θ, or expressed in notational form, $E(\hat{\theta}) = \theta$. Let $x_1, x_2, \ldots, x_n$ be a sample of n replicate method determinations. Then we define:

(1) $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$ as the *sample mean*, an unbiased estimate of the *true mean*, δ, *of the determinations*. This term gives an estimate of the center of the distribution of the x_i's.

(2) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2$ as the *sample variance*, an unbiased estimate of the *true variance*, σ^2. This term gives a measure of the dispersion in a distribution.

(3) $s = \sqrt{s^2}$ as the *sample standard deviation*, an alternative measure of dispersion, which estimates σ, *the true standard deviation*.

The sample standard deviation, s, however, is not unbiased for σ,[2] so a *correction factor* needs to be applied. The correction factor for a sample of size n from a normal population is α_n, and the product of α_n and s is unbiased for σ. That is, $E(\alpha_n s) = \sigma$. As n increases, the value of α_n decreases to eventually approach 1.0, going for example from $\alpha_3 = 1.1284$, $\alpha_4 = 1.0854$ to $\alpha_{10} = 1.0281$.

We define

$$\beta = \frac{\sigma}{\delta}$$

as the *true coefficient of variation* for the distribution of the method determinations. To estimate this parameter, we use a *sample coefficient of variation*, $\hat{\beta}$, defined by

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

where $\hat{\beta}$ is the ratio of the unbiased estimates of σ and δ, respectively. The coefficient of variation measures the percentage scatter in the observations about the mean and thus is a readily understandable way to express the precision of the observations.

The collaborative test plan for this test called for 16 *runs*. On each run, the collaborative teams were expected to collect simultaneous samples from the stack in accordance with Method 5. Since the actual particulate emission concentration in the stack fluctuates, one can generally expect different true concentrations for each run. To permit a complete statistical analysis, the individual runs are grouped into *blocks*, where each block has approximately the same true emission concentration level.

We can apply the statistical terms of the preceding paragraph both to the collaborators' values during a given run, and to each collaborator's values in a given block. In this report, statistical results from the first situation are referred to as *run results*. Those from the second situation are referred to as *collaborator block results*. For example, a run mean is the average of each collaborator's concentration level for the run as obtained by Method 5. A collaborator block coefficient of variation is the ratio of the unbiased standard deviation estimate to the sample mean for all of a collaborator's runs grouped in the block.

The variability associated with a Method 5 concentration determination is estimated in terms of the *within-laboratory* and the *between-laboratory precision components*. In addition, a *laboratory bias component* can be estimated. The following definitions of these terms are given with respect to a *true stack concentration*, μ:

- *Within-laboratory*—The within-laboratory standard deviation, σ, measures the *dispersion in replicate single determinations* made using Method 5 by one laboratory team (same field operators, laboratory analyst, and equipment) sampling the same true concentration, μ. The value of σ is estimated from within each collaborator block combination.

- *Between-laboratory*—The between-laboratory standard deviation, σ_b, measures the *total variability in a concentration determination* due to simultaneous Method 5 determinations by different laboratories sampling the same true stack concentration, μ. The between laboratory variance, σ_b^2, may be expressed as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2$$

  and consists of a within-laboratory variance plus a *laboratory bias variance*, σ_L^2. The between-laboratory standard deviation is estimated using the run results.

- *Laboratory bias*—The laboratory bias standard deviation, $\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$, is that portion of the total variability that can be ascribed to differences in the field operators, analysts and instrumentation, and due to different manners of performance of procedural details left unspecified in the method. This term measures that part of the total variability in a determination which results from the use of the method by different laboratories, as well as from modifications in usage by a single laboratory over a period of time. The laboratory bias standard deviation is estimated from the within- and between-laboratory estimates previously obtained.

B. The Experimental Design

The collaborative test of Method 5 at the Lone Star Industries' Cement Plant in Houston, Texas was conducted on the kiln stack under ambient operating conditions. No attempt was made to block the concentration of the particulate matter emitted from the stack into distinct levels. Of a planned 16 sampling runs, 15 were actually conducted, at a rate of one or two runs per day. A run involved 2 hours of simultaneous sampling by each of the four collaborators. Approximately one-fourth of a run's sample, which consisted of 30 min of sampling, was collected at each of the four ports by each collaborator. At each port, the collaborator made a radius traverse of the circular stack, sampling for six minutes each from the five traverse points according to Method 1. Table 1 shows the layout of the test. The starting port for each collaborator, and the direction of port rotation during the run, were randomized each day. When two runs were made on the same day, sampling on the second run was rotated in the opposite direction of the first run, avoiding entanglement of the umbilical cords connecting the sampling equipment to the control consoles.

Table 1. Design of the Cement Plant Collaborative Test of Method 5

Day	Run	Rotation Direction*	Final Port Sampled			
			Lab 101	Lab 102	Lab 103	Lab 104
4/2/73	1	Ccl.	C	A	D	B
4/3/73	2	Ccl.	B	D	C	A
4/4/73	3	Ccl.	B	A	C	D
4/5/73	4	Cl.	C	B	D	A
	5	Ccl.	B	A	C	D
4/6/73	6	Ccl.	B	A	C	D
4/9/73	7	Cl.	D	C	A	B
	8	Ccl.	A	D	B	C
4/10/73	9	Ccl.	A	D	B	C
	10	Cl.	B	A	C	D
4/11/73	11	Ccl.	D	A	B	C
	12	Cl.	A	B	C	D
4/12/73	13	Cl.	A	B	C	D
	14	Ccl.	A	B	C	D
4/13/73	15	Cl.	C	B	D	A

*Cl. –The laboratory teams sampled from the four ports clockwise around the stack.
Ccl.–Sampling was conducted counterclockwise around the stack.

Because the runs were conducted under ambient operating conditions, with no intention of holding the particulate concentration constant from run to run, one would expect some drift in the true average particulate concentration in the stack from run to run. In fact, the run particulate concentrations varied from around 8×10^{-7} lb/scf to 60×10^{-7} lb/scf.* Some of this run variation may be attributed to the curtailment from capacity three kiln operation on the first week of the collaborative test to a two kiln operation on the second week. However, the in-plant bolometer indicated that the preponderance of the run variation resulted from sporadic upset conditions during the testing periods. Even if the runs were grouped into blocks of approximately equivalent concentration levels, some variation in the true concentration could still be expected for the runs in a block. Hence, in order to estimate the within-laboratory precision variability of Method 5, it is likely that the particulate concentration data will have to be adjusted for true variation from one run to another.

Particulate matter will precipitate out of any particulate-air or particulate-acetone mixture. Therefore, one cannot prepare a known particulate concentration in air for conducting a Method 5 accuracy test; nor can one prepare a known particulate solution in acetone for use in determining

*EPA policy is to express all measurements in Agency documents in metric units. When implementing this policy will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular nonmetric units used in the document. For this report, the factors are:

10^{-7} lb/scf = 1.6018×10^{3} $\mu g/m^3$
1 scf = 0.028317 m^3
1 in. = 0.0254 m

the precision of just the analytical phase of Method 5. Consequently, *this collaborative test report cannot assess the accuracy of Method 5, nor can it separate Method 5 precision variability into its sampling phase and analysis phase components.*

C. The Collaborative Test Data

The essential Method 5 data that were originally reported by the four participating laboratories in this collaborative test are displayed in Table 2. Shown in Table 2 are c, the Method 5 particulate matter concentration, I, the percent of isokinetic sampling, and $V_{m\,std}$, the volume of gas sampled corrected to standard conditions (70°F, 29.92 in. Hg), reported by each collaborator for each run. I is tabulated because the acceptable isokinetic sampling range for Method 5 is $90\% \leq I \leq 110\%$ (cf. Appendix A). $V_{m\,std}$ is presented because a minimum sampling volume of 60 scf corrected to standard conditions on a dry basis is specified in the *Federal Register*[3] for Portland cement plants. Note that many of the runs fail to meet one or both of these criteria. There are three missing data points. Lab 101 incurred a leak causing loss of vacuum on Run 14. Lab 102 had to abort on Run 5 because a power failure caused water to surge into the filter holder; this necessitated replacing the filter. Some of the equipment used by Lab 103 was malfunctioning during Run 1.

There are wide discrepancies in the collaborators' particulate concentration values for a single run, with one collaborator's concentration frequently differing from another's by an order of magnitude or more. Lab 103 was especially prone to discrepant reported concentrations. Discussion with Lab 103 personnel, including an on-site review of their analytical procedures, revealed that *Lab 103 was performing Texas' Rule 9 rather than EPA's Method 5 to determine particulate matter concentration.* The procedure used by Lab 103 involves extraction of condensibles from the impinger catch. The extracts are added to the acetone probe and glassware wash before evaporation. Therefore, the combined probe catch and extracted condensibles are obtained and reported. Since these methods are incompatible, it is impossible to convert Rule 9 concentrations into their Method 5 equivalent. Consequently, *Lab 103 had to be excluded from the entire data analysis.*

According to the customary procedure, the calculations of the outlying sample concentrations reported by the three remaining collaborators were rechecked. Numerous sizable calculation errors were discovered that cast doubt on the validity of all the reported data in Table 2. Therefore, all the calculations involved in computing $V_{m\,std}$, c, and I were done over from the raw data for every run of the three remaining collaborators. The corrected data are presented in Table 3.

In the process of recalculation, numerous Method 5 errors were encountered. Section B.1 of Appendix B describes the calculation errors in detail. The most disturbing mistakes were made by using the wrong sets of data and using one wrong formula, in addition to excessive rounding on intermediate steps of calculations. Table 3 shows that the reported Table 2 values were frequently in error by as much as 10 percent due to improper calculation. Thus, *calculation is a major source of error in the use of Method 5.*

There are two ways to remedy the calculation errors that plague the usage of Method 5 and the associated Methods 2 and 3 that it requires. One approach is to design a standard data form on which all of the raw data required in the calculations of Methods 2, 3, and 5 could be recorded for easy keypunching. The keypunched data could then be input to a computer program to perform

Table 2. The Collaborators' Original Reported Data for the Cement Plant Collaborative Test of Method 5

Run	Lab 101			Lab 102			Lab 103			Lab 104		
	c	I	$V_{m_{std}}$	c	I	$V_{m_{std}}$	c	I	$V_{m_{std}}$	c	I	$V_{m_{std}}$
1	15	111.3	63.2	12.9	108	80.9	Missing	–	–	14.2	112.0	66.4
2	13	114.3	63.7	13.1	103	80.2	43.5	103	69.2	11.8	120.1	77.3
3	11	113.0	63.5	10.3	109	83.9	71.2	90.9	84.0	11.2	97.5	70.6
4	150	117.7	58.6	18.8	106	76.2	83.3	97.6	63.0	9.2	132.4	86.7
5	11	106.3	53.4	Missing	–	–	130.3	97.7	61.7	10.6	112.4	67.3
6	8.8	108.7	58.2	8.6	107	74.8	79.0	97.6	62.8	8.2	108.3	68.3
7	18	96.3	53.4	15.3	87	69.4	202.9	91.8	59.5	9.4	99.7	78.1
8	29	104.0	58.6	15.9	92	77.1	270.8	91.1	62.1	14.4	107.2	77.3
9	150	102.7	58.4	6.8	101	79.5	128.6	95.0	66.7	9.0	108.3	73.5
10	140	106.0	58.9	12.3	98	77.0	39.3	97.6	67.2	9.4	109.4	70.5
11	29	107.3	58.7	20.7	106	74.5	54.3	102	65.2	17.4	105.7	65.1
12	33	108.0	58.7	38.9	103	77.7	71.0	101	65.0	23.6	107.7	66.0
13	230	109.7	58.5	75.2	103	75.4	80.4	98.9	64.0	57.8	96.3	61.2
14	Missing	–	–	19.8	99	67.9	42.2	102	60.3	10.5	105.9	59.4
15	27	103.7	53.4	26.9	102	72.1	98.9	101	62.1	18.7	110.4	64.6

Note:
c–Particulate matter concentration from Method 5, 10^{-7} lb/scf.
I–Percent of isokinetic sampling.
$V_{m_{std}}$–Volume of gas sample at standard conditions, cu. ft.

Table 3. The Corrected Data for the Cement Plant Collaborative Test of Method 5

Run	Lab 101			Lab 102			Lab 104		
	c	I	$V_{m_{std}}$	c	I	$V_{m_{std}}$	c	I	$V_{m_{std}}$
1	16.0	96.8	63.7	12.9	108.8	80.9	13.1	107.8	72.4
2	14.5	100.5	64.0	13.1	102.7	80.2	11.8	115.2*	77.2
3	12.4	99.5	64.4	10.3	108.8	83.9	10.9	101.2	72.1
4	137.0†	108.2	62.4	18.8	106.1	76.2	11.7	111.1*	67.9
5	10.8	101.4	58.2‡	Missing	–	–	10.7	113.8*	66.5
6	10.5	99.1	59.5‡	8.6	107.0	74.8	7.8	114.0*	71.1
7	17.0	89.2*	57.0‡	15.3	87.0*	69.4	9.4	100.6	73.2
8	29.2	90.1	59.2‡	15.9	92.6	77.1	15.5	108.4	71.6
9	148.8†	103.6	58.4‡	6.8	100.6	79.6	9.0	109.5	73.5
10	137.4†	93.5	61.5	12.3	98.0	76.6	6.3	110.9*	70.4
11	28.7	98.3	60.6	20.7	101.6	74.5	15.7	115.8*	72.1
12	33.4	97.7	60.7	38.9	103.4	77.8	21.2	117.3*	73.3
13	214.2†	99.9	61.7	75.3	102.8	75.3	52.2	107.4	67.9
14	Missing	–	–	19.8	99.4	68.0	9.5	115.2*	65.6
15	27.0	99.5	56.4‡	26.9	102.2	72.1	18.9	111.6*	64.1

Note:
c–Particulate matter concentration from Method 5, 10^{-7} lb/scf.
I–Percent of isokinetic sampling.
$V_{m_{std}}$–Volume of gas sample at standard conditions, scf.

*Outside acceptable isokinetic sampling range: $90 < I < 110$.
†High concentration; probable probe tip particulate scraping from stack wall.
‡Less than minimum sampling volume of 60 cu. ft.

all the calculations and print the necessary results. This would eliminate calculation errors. However, there are difficulties to implementing this approach. Most available equipment does not measure in the desired metric units. Voluminous data are obtained on every sample. Finally the number of traverse points is not fixed but will vary from one site to another. An alternative approach is to clarify the calculation procedures of Methods 2 and 5. The formulas and data sources for all variables calculated in these methods should be stated explicitly. Furthermore, a note of caution should be added warning against intermediate rounding of calculations. The analyst should retain at least one more significant digit on all intermediate calculation steps than he intends to report in his results.

A perusal of the Table 3 particulate matter concentration data obtained by Method 5 reveals four values, all of which appear to be approximately one order of magnitude too high. These high concentration samples were all obtained by Lab 101, on Runs 4, 9, 10, and 13. Because no violation of the Method 5 procedures could be found, there are no physical grounds for rejecting these high concentrations. They must be treated as valid Method 5 determinations. But because these four high determinations are certain to cause most of the Method 5 precision variability reported for this test, it is essential to seek an explanation for their occurrence.

In all three of the Method 5 collaborative tests that have been conducted, high particulate matter concentrations have occurred. An analysis of the 12 high concentrations that occurred in the three tests is presented in Section B.2 of Appendix B. In 11 of the 12 cases, the high concentration is due to an excessive amount of particulate matter, ranging from 310 mg to 860 mg, present in the acetone washings of all sample-exposed surfaces prior to the filter. The probable explanation is that the probe tip was scraped against the inner stack wall during the insertion or removal of the sampling train from one of the sampling ports on these runs; this scraping would contaminate the probe tip with the particulate adhering to the wall. Subsequent sampling during the run might suck the contaminating particulate material into the probe body or through it to the filter. Apparently, *the principal cause of the high particulate concentration phenomenon that has afflicted all three Method 5 collaborative tests is accidental scraping of the probe tip against the stack wall* while the probe is being inserted into or removed from the stack.

Table 3 lists 43 Method 5 particulate concentration determinations. Four of these determinations, those followed by a dagger(†), are the high values. All four of these high values were obtained by Lab 101—on Runs 4, 9, 10, and 13. Since these appear to be valid Method 5 determinations, they should be included with the other determinations in evaluating the precision of Method 5. However, many auxiliary aspects of Method 5 and this collaborative test are also investigated in the statistical analysis. Since the magnitude of the high value effect usually obliterates the finer effects of these other aspects, the four high determinations are generally eliminated from the data for these side analyses.

Method 5 stipulates that the isokinetically acceptable sampling range is $90 \leq I \leq 110$. For 11 of the 43 samples shown in Table 3, I lies outside the acceptable range. But a single laboratory, Lab 104, obtained 9 of these 11 isokinetically unacceptable samples. Lab 104 reports that its isokinetic sampling problem probably arose from using an old wet test meter, subsequently found to be inaccurate, to calibrate its dry gas meter. Using this inaccurate primary standard meter may have given inaccurate calibration constants both for the nomograph setting and for the dry gas meter correction factor. Hence, the frequent failure to maintain isokinetic sampling on this collaborative test does not suggest any general difficulty in adhering to the restriction $90 \leq I \leq 110$. Now, of course, the 11 isokinetically unacceptable concentration samples have to be excluded from the analysis of Method 5 precision. But because there are so few determinations per run with Lab 103

excluded, the isokinetic restriction is sometimes relaxed to $85 \leq I \leq 115$ or $80 \leq I \leq 120$ in the side analyses in order to provide sufficient data for a substantive treatment.

The corrected dry gas volume sampled is below the *Federal Register* limitation of $V_{m\ std} \geq 60$ scf on six of the 43 samples, all of which were obtained by Lab 101. Enforcement of this minimum sampling volume condition, in addition to the isokinetic acceptance condition, with Lab 103 excluded, would have left too little data on which to base a meaningful analysis of the Method 5 precision. The minimum sample volume condition is never violated by more than 10 percent. Consequently, this volume condition is considered the least vital of the data exclusion criteria, and it is ignored in nearly all of the statistical analysis.

In taking its 2-hour sample by Method 5 on a run of this collaborative test, each collaborator was supposed to sample isokinetically for 30 min from each of the four ports. Normally, one would not expect a port effect influencing the data under these circumstances. Yet due to the probable probe tip contamination discussed above, an analysis of the final port effect was made. This analysis is conducted in Section B.3 of Appendix B. No final port effect is detected in the Method 5 samples by Youden's Rank Test. It can be concluded that the final port from which a collaborator sampled had no systematic effect on his Method 5 concentration determination.

However, *the true particulate concentration sampled did vary greatly from one run to another during the collaborative test*. For example, the average of the acceptable collaborators' Method 5 particulate concentration determinations sampled, with high values eliminated, is 7.9×10^{-7} lb/scf on Run 9, 11.2×10^{-7} lb/scf on Run 3, 24.7×10^{-7} lb/scf on Run 11, and 63.8×10^{-7} lb/scf on Run 13. In Section B.4 of Appendix B, the Kruskal-Wallis H Test is applied to the acceptable determinations. The H Test shows that the variation in the true particulate concentration from one run to another during the collaborative test is indeed significant.

The effect of the tremendous variation in the true particulate concentration from run to run must be removed from the collaborative test data prior to estimating the within-laboratory precision. Otherwise, the calculated within-laboratory precision would be greatly inflated. Several statistical techniques can be employed to remove this true concentration effect. In Section B.4 of Appendix B, the runs having roughly the same true particulate concentration are grouped into blocks. The runs are ranked in ascending order of predicted true particulate concentration according to their in-stack bolometer opacity charts and the daily feedrate. Then the runs in the same rank score range are assigned to the same block. Runs 9, 3, 1, 10, 5, 6, 2, and 7 with rank scores ranging from 11.5 to 27.0 are placed in Block 1. Runs 4, 11, 14, 8, 12, and 15 having rank scores from 32.0 to 50.0 are assigned to Block 2. Run 13 with a rank score of 57.5 is given a separate block, Block 3. Table B-5 in Appendix B illustrates the blocking assignment of each run based on its rank score.

Blocking the runs does remove much of the true concentration effect, but not all of it. The analysis of Section B.5 of Appendix B demonstrates that there is considerable variation in the true particulate matter concentration of the runs grouped in the same block. This variation is substantial enough to overwhelm the sensitive statistical procedure used to separate the between-laboratory variance into its within-laboratory and laboratory-bias components. Calculation by the usual procedure yields no laboratory bias in the collaborative test data. On the other hand, simple inspection of the test data and statistical analysis by laboratory using Youden's Rank Test both reveal a large laboratory bias effect. To reconcile the calculation procedure results with the evident nature of the test data, the variation in true concentration among the runs in the same block must be separated from the method's actual precision variation and eliminated. In the absence of any alternative indicator of the true particulate concentration, the collaborators' Method 5 run mean is

used as the true concentration indicator. The true concentration effect is removed from the blocks by adjusting every collaborator's determination on a run by the amount needed to give the run the same mean as its block. The resulting adjusted data is shown in Table B-8 of Appendix B. While this data adjustment technique probably over-adjusts the within-laboratory precision estimates, it does permit the calculation of a laboratory-bias precision component of reasonable magnitude in comparison with the corrected concentration data of Table 3.

D. The Precision of Method 5

The precision of Method 5 at cement plants is examined in two situations. The first situation relates to Method 5 as published in Appendix A: the high particulate concentration phenomenon occurs occasionally, the stated isokinetic sampling restriction ($90 \leq I \leq 110$) is enforced, and approximately 60 scf of dry gas is sampled ($V_{m\,std} \geq 56$ scf). The resultant acceptable data from Table 3 under these restrictions are displayed in Table 4, with a run summary included. The four runs with high values stand out sharply from the other runs in Table 4. These four runs have standard deviations ranging from 81.4×10^{-7} lb/scf to 88.5×10^{-7} lb/scf, while the maximum for the other runs is only 7.8×10^{-7} lb/scf.

Table 4. The Corrected Data for Between-Laboratory Analysis of the Published Version of Method 5

Block	Run	Acceptable Method 5 Particulate Concentration Determinations, 10^{-7} lb/scf			Run Summary			
		Lab 101	Lab 102	Lab 104	Mean, $\bar{x}_j$	Standard Deviation, s_j	Coef. of Variation, $\hat{\rho}_j$	Weight, W_j
	9	148.8	6.8	9.0	54.87	81.36	1.6732	1.366
	3	12.4	10 3	10.9	11.20	1.08	0.1090	1.366
	1	16.0	12.9	13.1	14.00	1.73	0.1398	1.366
1	10	137.4	12.3	R	74.85	88.46	1.4812	0.738
	5	10.8	M	R	10.80			
	6	10.5	8.6	R	9.55	1.34	0.1763	0.738
	2	14.5	13.1	R	13.80	0.99	0.0899	0.738
	7	R	R	9.4	9.40			
	4	137.0	18.8	R	77.90	83.58	1.3447	0.738
	11	28.7	20.7	R	24.70	5.66	0.2870	0.738
	14	M	19.8	R	19.80			
2	8	29.2	15.9	15.5	20.20	7.80	0.4355	1.366
	12	33.4	38.9	R	36.15	3.89	0.1348	0.738
	15	27.0	26.9	R	26.97	0.07	0.0033	0.738
3	13	214.2	75.3	52.2	113.90	87.63	0.8681	1.366

Note:
M–Missing determination.
R–Rejected determination: outside acceptable isokinetic sampling range, $90 \leq I \leq 110$.

It is felt that Method 5 can be improved to eliminate some, and perhaps most, of the high particulate concentration phenomenon. To assess the impact of this improvement on Method 5's precision, a second situation is also considered. The $90 \leq I \leq 110$ isokinetic sampling restriction is retained, and a loose $V_{m\,std} \geq 56$ scf interpretation of the minimum sampling volume limitation is again taken. But now the four high particulate concentrations are excluded from the valid collaborative test data. Table 5 presents the collaborative test data for this second situation and its run summary. Here the standard deviations and the coefficients of variation for the runs are much more uniform.

Table 5. The Corrected Data for Between-Laboratory Analysis of Method 5 Improved to Eliminate the High Value Phenomenon

Block	Run	Acceptable Method 5 Particulate Concentration Determinations with High Values Excluded, 10^{-7} lb/scf			Run Summary			
		Lab 101	Lab 102	Lab 104	Mean, $\bar{x}_j$	Standard Deviation, s_j	Coef. of Variation, $\hat{\beta}_j$	Weight W_j
1	9	E	6.8	9.0	7.90	1.56	0.2468	0.797
	3	12.4	10.3	10.9	11.20	1.08	0.2090	1.474
	1	16.0	12.9	13.1	14.00	1.73	0.1398	1.474
	10	E	12.3	R	12.30			
	5	10.8	M	R	10.80			
	6	10.5	8.6	R	9.55	1.34	0.1763	0.797
	2	14.5	13.1	R	13.80	0.99	0.0899	0.797
	7	R	R	9.4	9.40			
2	4	E	18.8	R	18.80			
	11	28.7	20.8	R	24.70	5.66	0.2870	0.797
	14	M	19.8	R	19.80			
	8	29.2	15.9	15.5	20.20	7.80	0.4355	1.474
	12	33.4	38.9	R	36.15	3.89	0.1348	0.797
	15	27.0	26.9	R	26.95	0.07	0.0033	0.797
3	13	E	75.3	62.2	63.75	16.33	0.3211	0.797

Note:

E–Excluded determination: high value concentration probably caused by scraping probe tip against stack wall.

M–Missing determination.

R–Rejected determination: outside acceptable isokinetic sampling range, $90 \leq I \leq 110$.

As discussed in the previous section and in Section B.5 of Appendix B, data adjustment is necessary to eliminate the true concentration effect and thus to permit a valid within-laboratory precision analysis. Because the effect of the high value phenomenon obscures all finer effects, data adjustment is applied to the Table 5 data, in which the high values are excluded, to yield the appropriate data for the within-laboratory analysis. Table 6 presents the adjusted data and gives a statistical summary for each collaborator block that is the basis of the within-laboratory analysis.

A weighted coefficient of variation approach is used to obtain the precision estimates for Method 5 at cement plants. This procedure is only valid when the collaborative test data exhibit a proportional relationship between the standard deviation and the mean. There are two essential proportional relationships: that between laboratories over the test runs and that within each laboratory on the collaborator's blocked samples adjusted to replication conditions. The Table 4 and Table 5 run summaries provide the between-laboratory mean and standard deviation data for the two situations under consideration. The corresponding within-laboratory mean and standard deviation data for each collaborator block, which is appropriate for both situations, are shown in Table 6. Graphical and more sophisticated statistical techniques are employed in Section B.6 of Appendix B to examine these relationships of standard deviation to mean. The examination yields enough favorable evidence to warrant the conclusion that the proportionality of standard deviation to mean is characteristic of Method 5 concentration determinations at cement plants, both between laboratories and within a single laboratory.

The precision estimates obtained for Method 5 at cement plants are summarized in Table 7 for both situations. These estimates are derived by the weighted coefficient of variation approach in Section B.8 of Appendix.B.

Table 6. The Adjusted Data for Within-Laboratory Analysis of Method 5

Block	Collaborator	Acceptable Adjusted Method 5 Particulate Concentration Determinations with High Values Excluded, 10^{-7} lb/scf — Runs in the Block								Collaborator Block Summary			
										Mean, $\bar{x}_{i,k}$	Standard Deviation, $s_{i,k}$	Coef. of Variation, $\hat{\beta}_{ik}$	Weight, w_{ik}
1		1	2	3	4	5	6	7	8				
	Lab 101	E	12.3	13.2	E	11.1	12.1	11.8	R	12.10	0.76	0.0672	1.000
	Lab 102	10.0	10.2	10.0	11.1	M	10.2	10.4	R	10.32	0.41	0.0420	1.231
	Lab 104	12.2	10.8	10.2	R	R	R	R	11.1	11.07	0.84	0.0821	0.769
2		9	10	11	12	13	14						
	Lab 101	E	28.4	M	33.4	21.7	24.5			27.00	5.07	0.2040	0.769
	Lab 102	24.4	20.4	24.4	20.1	27.2	24.4			23.48	2.73	0.1222	1.231
	Lab 104	R	R	R	19.7	R	R			19.70			
3		15											
	Lab 101	E											
	Lab 102	75.3								75.30			
	Lab 104	52.2								52.20			

Note:
E–Excluded determination: high concentration probably caused by scraping probe tip against stack wall.
M–Missing determination.
R–Rejected determination: outside acceptable isokimetic sampling range, $90 < I < 110$.

Table 7. Method 5 Precision Estimates for the Published Version and for a Hypothetical Version Modified to Eliminate the High Value Phenomenon

Situation		Precision Measure	Coefficient of Variation, $\hat{\beta}$	Standard Deviation, $\hat{\sigma}$
Criterion	Value			
Application:	Published Method 5	Between Labs	$\hat{\beta}_b = 0.584$	$\hat{\sigma}_b = (0.584)\delta$
Site:	Portland Cement Plants	Within Labs	$\hat{\beta} = 0.284$	$\hat{\sigma} = (0.284)\delta$
Data Characteristics:		Lab Bias	$\hat{\beta}_L = 0.510$	$\hat{\sigma}_L = (0.510)\delta$
High Values	Included			
Isokinetic Restriction	$90 < I < 110$			
Min. Volume Limit	56 scf			
Data Sources:	Tables 4 and 6			
Application:	Method 5 Modified to Eliminate High Value Phenomenon	Between Labs	$\hat{\beta}_{b(e)} = 0.201$	$\hat{\sigma}_{b(e)} = (0.201)\delta$
		Within Labs	$\hat{\beta}_{(e)} = 0.098$	$\hat{\sigma}_{(e)} = (0.098)\delta$
		Lab Bias	$\hat{\beta}_{L(e)} = 0.176$	$\hat{\sigma}_{L(e)} = (0.176)\delta$
Site:	Portland Cement Plants			
Data Characteristics:				
High Values	Excluded			
Isokinetic Restriction	$90 < I < 110$			
Min. Volume Limit	56 scf			
Data Sources:	Tables 5 and 6			

The precision estimates for Method 5 as written, the situation in which the high value phenomenon occasionally occurs, are presented in the upper half of Table 7. The between-laboratory coefficient of variation β_b is estimated as the weighted average of the run coefficients of variation shown in Table 4. The run coefficient of variation weights are assigned based on the number of collaborators making a determination on the run (cf. Section B.7 of Appendix B). The weighted average is $\beta_b = 0.584$, with a maximum of 3 participating collaborators per run. Let δ denote the true particulate concentration

in a cement plant stack at which Method 5 particulate determinations are made. *The estimated between-laboratory standard deviation is $\sigma_b = (0.584)\delta$ with 2 degrees of freedom.* With so few degrees of freedom, the true between-laboratory values could vary markedly from these estimates. The within-laboratory coefficient of variation is estimated via a weighted average of the collaborator-block coefficients of variation in Table 6, with an adjustment to reintroduce the high value effect (cf. Section B.8 of Appendix B). A within-laboratory coefficient of variation of $\hat{\beta} = 0.284$ is obtained. This gives an *estimated within-laboratory standard deviation of $\hat{\sigma} = (0.284)\delta$, which has no more than 2 degrees of freedom* because the adjustment involves the ratio $(\hat{\beta}_b/\hat{\beta}_{b(e)})$ of between-laboratory precision estimates each of which have only 2 degrees of freedom. The concomitant laboratory bias standard deviation estimate is $\hat{\sigma}_L = (0.510)\delta$.

Method 5 precision estimates are also obtained for a second situation, which assumes the development of a hypothetical version of Method 5 that could prevent the high value phenomenon from occurring. These precision estimates, which are obtained from the Table 5 run summary and the Table 6 collaborator block summary, are shown in the lower half of Table 7. If the high value phenomenon could be eliminated from Method 5, the estimated between-laboratory standard deviation would be $\sigma_{b(e)} = (0.201)\delta$, and the estimated within-laboratory standard deviation $\sigma_{(e)} = (0.098)\delta$. The subscript e denotes elimination of the high value phenomenon. *Preventing the high value phenomenon from affecting Method 5 would tremendously improve the method's precision in measuring the particulate matter concentration at cement plants.*

One should exercise caution in the use of the precision estimates shown in Table 7. The between-laboratory estimates are based on a maximum of 3 collaborators' determinations per run, and thus they only possess 2 degrees of freedom. The published Method 5 within-laboratory estimates are calculated using these between-laboratory estimates and thus also have just 2 degrees of freedom. The entire population of laboratories performing Method 5 might differ substantially from the three laboratories, Labs 101, 102, and 104, employed in this cement plant collaborative test. Hence *it is quite conceivable that the true between-laboratory, within-laboratory, and laboratory bias standard deviations for Method 5 might vary from the estimates shown in Table 7 for cement plant applications by a factor of 2 in either direction.* Since the hypothetical version's within-laboratory estimates have 20 degrees of freedom, these estimates are more precise. It should also be noted that real world collaborative testing places some extraordinary burdens on the collaborative teams that result from sampling in cramped quarters on a fairly rigid schedule for long hours every work day for two consecutive weeks. These burdens, which would not be experienced in compliance testing of the method, would tend to cause additional operator errors and to thereby inflate the precision estimates above the true precision of the method.

E. Sources of Variability in a Method 5 Test Result

The preceding section has disclosed that the lack of precision appears to be a major weakness in the published version of Method 5, at least for its cement plant applications. The between-laboratory standard deviation associated with a particulate concentration determination at a cement plant is more than half as large as the true value of the determination itself. The other two Method 5 collaborative tests[4,5] reveal that imprecision is also a deficiency of Method 5 in fossil fuel-fired steam generators and in incinerators. This section will analyze many of the sources of variability in the estimated cement plant between-laboratory and within-laboratory standard deviations.

As Table 3 shows, the cement plant collaborative test yielded many questionable or unacceptable Method 5 samples (non-isokinetic sampling,deficient volume sampling, and/or high particulate concentration determinations). Hence, the cement plant test offers a rare opportunity to evaluate these sources under field conditions as contributors to the between-laboratory and within-laboratory

precision variability in a Method 5 determination. One approach to ascertaining whether a given factor is a source of variation is to compare the between- and within-laboratory standard deviations calculated by a weighted coefficient of variation analysis, when the factor is allowed against the comparable standard deviations, for the published Method 5, in which the factor is not allowed. This approach is applied to the high value phenomenon, the isokinetic sampling restriction, and the minimum sampling volume limitation. The results are reported in Table 8.

Table 8. The Effects of Eliminating the High Value Phenomenon and Relaxing the Isokinetic Sampling and Minimum Sampling Volume Restructions

Data Base			Between-Lab Standard Deviation		Within-Lab Standard Deviation	
Use of High Values	Isokinetic Sampling Restriction	Minimum Sampling Volume Limit	Estimated Value $\hat{\sigma}_b$	Percent Change from Current Restriction	Estimated Value $\hat{\sigma}$	Percent Change from Current Restriction
High Value Phenomenon						
Included	$90 \leq I \leq 110$	56 scf	$(0.584)\delta$	–	$(0.284)\delta$	–
Excluded	$90 \leq I \leq 110$	56 scf	$(0.201)\delta$	−66%	$(0.098)\delta$	−66%
Isokinetic Sampling Restriction – With High Values Included						
Included	$90 \leq I \leq 110$	56 scf	$(0.584)\delta$	–	$(0.284)\delta$	–
Included	$85 \leq I \leq 115$	56 scf	$(0.596)\delta$	+2%	$(0.360)\delta$	+27%
Included	$80 \leq I \leq 120$	56 scf	$(0.575)\delta$	−2%	$(0.317)\delta$	+ 8%
Isokinetic Sampling Restriction – High Values Eliminated						
Excluded	$90 \leq I \leq 110$	56 scf	$(0.201)\delta$	–	$(0.098)\delta$	–
Excluded	$85 \leq I \leq 115$	56 scf	$(0.244)\delta$	+21%	$(0.147)\delta$	+50%
Excluded	$80 \leq I \leq 120$	56 scf	$(0.275)\delta$	+37%	$(0.151)\delta$	+55%
Minimum Sampling Volume Restriction						
Excluded	$80 \leq I \leq 120$	60 scf	$(0.270)\delta$	–	$(0.158)\delta$	–
Excluded	$80 \leq I \leq 120$	56 scf	$(0.275)\delta$	+1%	$(0.151)\delta$	− 4%

The high value phenomenon is examined by comparing the between-laboratory standard deviation $\hat{\sigma}_{b\,(e)} = (0.201)\delta$ and the within-laboratory standard deviation $\hat{\sigma}_{(e)} = (0.098)\delta$ estimated for the second situation discussed in the previous section (high values excluded, $90 \leq I \leq 110$, $V_{m\,std} \geq 56$ scf) against the corresponding estimated values, $\hat{\sigma}_b = (0.584)\delta$ and $\hat{\sigma} = (0.284)\delta$, for the published Method 5 situation (high values included, $90 \leq I \leq 110$, $V_{m\,std} \geq 56$ scf). As Table 8 shows, this comparison reveals that an estimated 66 percent reduction in the precision standard deviations would occur if the high value phenomenon could be prevented.

The effect of relaxing the isokinetic sampling restriction is shown in Table 8 both when the high value phenomenon occurs and when it is eliminated. When the high value samples are excluded from the data, both the between-laboratory and the within-laboratory precision estimates undergo pronounced deterioration as the isokinetic restriction is relaxed from $90 \leq I \leq 110$ to $85 \leq I \leq 115$ and $80 \leq I \leq 120$. For example, the between-laboratory standard deviation estimate increases from $(0.201)\delta$ for $90 \leq I \leq 110$ to $(0.244)\delta$ for $85 \leq I \leq 115$ (+21 percent), to $(0.275)\delta$ for $80 \leq I \leq 120$ (+ 37 percent). Inclusion of the high sample values partially obscures this deterioration. There is still a 27 percent increase in the within-laboratory standard deviation estimate in relaxing from $90 \leq I \leq 110$ ($\hat{\sigma} = 0.284\delta$) to $85 \leq I \leq 115$ ($\hat{\sigma} = 0.360\delta$). But the high values obliterate the effect of isokinetic sampling relaxation on the between-laboratory precision. The

high value exclusion analysis demonstrates the necessity of maintaining the Method 5 isokinetic sampling restriction at $90 \leq I \leq 110$: any relaxation of this restriction will exacerbate the imprecision of Method 5.

To avoid confounding the effect of the minimum sampling volume restriction with the high value phenomenon effect, the minimum sampling volume restriction is only examined with the high values excluded. Table 8 shows that decreasing the minimum sampling volume limit from 60 scf to 56 scf when $80 \leq I \leq 120$ has little effect on either the between-laboratory or the within-laboratory standard deviation estimates. Apparently, samples falling slightly below the minimum sampling volume limit could be accepted without damaging the precision of Method 5.

Table 8 has shown that the high value phenomenon is the primary source of the between-laboratory variability in a determination obtained at a cement plant, according to the published version of Method 5. The portion of the between-laboratory variance caused by the high value phenomenon is the reduction in the between-laboratory variance excluding the high values compared against the between-laboratory variance calculated including them. These variance calculations are shown in Table 9. Over 88 percent of the between-laboratory variance in a concentration determination obtained by the published Method 5 at a cement plant is caused by the high value phenomenon. Only 11.9 percent of the between-laboratory variance results from all other sources. *If Method 5 is to be substantially improved, the cause of the high value phenomenon must be isolated and eliminated.* Based on the evidence of Section B-2 of Appendix B, we believe scraping the probe tip against the stack wall during insertion or removal of the sampling train is the cause of the high value phenomenon.

Table 9. Sources of Between-Laboratory Variation in a Method 5 Cement Plant Determination

Source of Between-Laboratory Variance	Estimated Variance Component	Percentage of Total Variance, %
Total Between-Laboratory, σ_b^2	$(0.3407)\delta^2$	100.0
• High Value Phenomenon	$(0.3002)\delta^2$	88.1
• All Other Sources, $\sigma_{b(e)}^2$	$(0.0405)\delta^2$	11.9
– Within Laboratory, $\sigma_{(e)}^2$	$(0.0096)\delta^2$	2.8
– Laboratory Bias, $\sigma_{L(e)}^2$	$(0.0309)\delta^2$	9.1

Table 9 also divides the between-laboratory variance from sources other than the high value phenomenon into its within-laboratory and laboratory bias components. This breakdown allots 9.1 percent of the between-laboratory variance to laboratory bias sources and 2.8 percent to within-laboratory sources. These percentages are 76 percent and 24 percent, respectively, of the other source variance. Since the within-laboratory analysis is based on a data adjustment technique that is probably too severe, it is probable that the actual percentage due to within-laboratory sources is between 30 and 35 percent, instead of the calculated 24 percent. However, even at 65 to 70 percent, the laboratory bias sources are still the major component of the other source variance. To improve Method 5 beyond eliminating the high value phenomenon, the main emphasis should be placed on further standardization of the method whenever possible so that each laboratory's performance of Method 5 is more similar.

IV. RECOMMENDATIONS

A number of problems relating to the precision and the usage of Method 5 in cement plant applications have been discussed in the Summary and Conclusions section. The following recommendations are made to alleviate these problems:

(1) The cement plant collaborative test appears to indicate that the precision of Method 5, both between laboratories and within a single laboratory, is poor. In addition, all of the laboratory teams participating in the collaborative test experienced difficulties using Method 5. In view of these facts, *the method should be rewritten.* The revised version of the method should incorporate the following suggestions or others that have the equivalent effect:

- Develop a procedure to prevent, or to at least inhibit, the occurrence of the high value phenomenon. This phenomenon is probably caused by accidentally scraping the probe tip against the particulate-laden stack wall while inserting or removing the probe through a sampling port. Thus a partial solution is to examine the probe tip for extraneous particulate matter each time it is removed from a port. However, if the scraping hypothesis is true, particulate could also be scraped into the tip while inserting the probe into a port, and sucked into the probe body or filter during the sampling at that port. To prevent or inhibit this, some redesign of the probe tip might be necessary.

- Standardize the method to reduce laboratory bias by specifying in greater detail how procedures are to be performed. To minimize the possibility of sample loss or contamination, both ends of the probe assembly prior to the filter should be capped as soon as the probe is extracted from the last sampling port. Specific instructions should be given for cleaning the probe assembly at the sample recovery area. Also, the equation for calculating the stack gas pressure P_s should be specified.

- Retain the isokinetic sampling restriction $90 \leq I \leq 110$. However, allow some latitude in the minimum dry gas sampling volume limitation. For instance, it might only be required that the average of the three test result samples' volumes exceed 60 scf, with each sample volume at least 50 scf. This latitude would ease somewhat the difficulty in obtaining acceptable Method 5 samples.

(2) After Method 5 is revised, it should be intensively field tested for reliability and ruggedness by an initiating laboratory, as Youden[6] recommends. The revised Method 5 should then be subjected to a thorough collaborative test, at one or more sites, to determine its precision and sources of variability.

(3) Thought should be given to developing standard data reporting forms suitable for keypunching and an accompanying computer program for the revised version of Method 5. The raw measurements from Methods 2, 3 and 5 would be recorded in specified units on the reporting forms, keypunched, and input to the computer program which would calculate the particulate matter concentration determination, the percent of isokinetic sampling, and the other necessary results. This procedure would eliminate the serious Method 5 calculation error problem, but it would be difficult to implement. Complicating factors include the lack of metric measuring equipment, the voluminous amount and variety of data collected on every sample, and the dependence of the number of traverse points, and hence, data points needed on the size and configuration of the stack cross section.

APPENDIX A

METHOD 5. DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

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4.2 Gas volume.

$$V_{m(std)} = V_m \left(\frac{P_{bar}}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right) = 17.71 \frac{°R}{in.\ Hg}\left(\frac{P_{bar}}{T_m}\right) \quad \text{equation 5-2}$$

where:

$V_{m(std)}$ = Dry gas volume through meter at [illegible], cu. ft.

V_m = Dry gas volume measured by meter, cu. ft.

P_{bar} = Barometric pressure at the dry gas meter, inches Hg.

P_{std} = Pressure at standard conditions, 29.92 inches Hg.

T_{std} = Absolute temperature at standard conditions, 528° R.

T_m = Absolute temperature at meter (°F + 460), °R.

4.3 Moisture content.

$$B_{wo} = \frac{V_{wc}}{V_{wc} + V_m} + B_{wa} = \frac{V_{wc}}{V_{wc} + V_{m(std)}} + (0.023) \quad \text{equation 5-3}$$

where:

B_{wo} = Proportion by volume of water vapor in the gas stream, dimensionless.

V_{wc} = Volume of water vapor collected (standard conditions), cu. ft.

$V_{m(std)}$ = Dry gas volume through meter (standard conditions), cu. ft.

B_{wa} = Approximate volumetric proportion of water vapor in the gas stream leaving the impingers, 0.023.

5. *References.*

Air Pollution Engineering Manual, Danielson, J. A. (ed.), U.S. DHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio, PHS Publication No. 999-AP-40, 1967.

Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif., November 1963.

Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases, Western Precipitation Division of Joy Manufacturing Co., Los Angeles, Calif., Bulletin WP-50, 1968.

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling train. The design specifications of the particulate sampling train used by EPA (Figure 5-1) are described in APTD-0581. Commercial models of this train are available.

2.1.1 Nozzle—Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe—Pyrex[1] glass with a heating system capable of maintaining a minimum gas temperature of 250° F. at the exit end during sampling to prevent condensation from occurring. When length limitations (greater than about 8 ft.) are encountered at temperatures less than 600° F. Incoloy 825[1], or equivalent, may be used. Probes for sampling gas streams at temperatures in excess of 600° F. must have been approved by the Administrator.

2.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter Holder—Pyrex[1] glass with heating system capable of maintaining minimum temperature of 225° F.

2.1.5 Impingers / Condenser—Four impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a ½-inch ID glass tube extending to one-half inch from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. A condenser may be used in place of the impingers provided that the moisture content of the stack gas can still be determined.

2.1.6 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5° F., dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer—To measure atmospheric pressure to ±0.1 inches Hg.

2.2 Sample recovery.

2.2.1 Probe brush—At least as long as probe.

2.2.2 Glass wash bottles—Two.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder—250 ml.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance—To measure to ±0.1 mg.

2.3.4 Trip balance—300 g. capacity, to measure to ±0.05 g.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber, MSA 1106 BH[1], or equivalent, numbered for identification and preweighed.

3.1.2 Silica gel—Indicating type, 6-16 mesh, dried at 175° C. (350° F.) for 2 hours.

3.1.3 Water.

3.1.4 Crushed ice.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade.

3.3 Analysis.

3.3.1 Water.

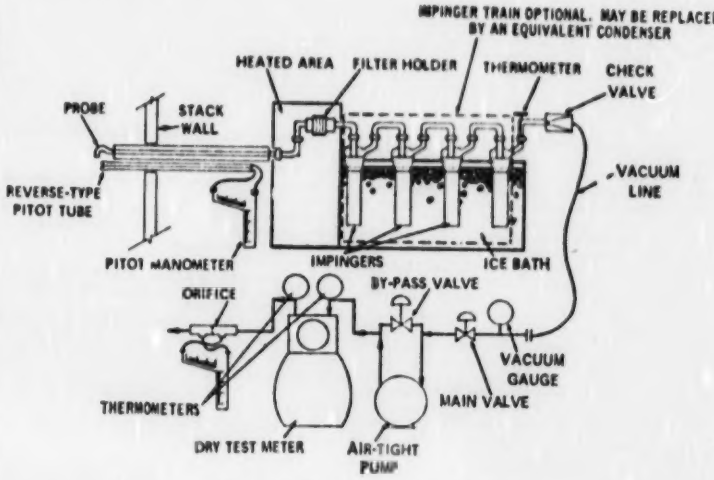

Figure 5-1. Particulate-sampling train.

3.3.2 Desiccant—Drierite[1] indicating.

4. *Procedure.*

4.1 Sampling.

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Weigh to the nearest gram approximately 200 g. of silica gel. Label a filter of proper diameter, desiccate[2] for at least 24 hours and weigh to the nearest 0.5 mg. in a room where the relative humidity is less than 50%. Place 100 ml. of water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g. of preweighed silica gel in the fourth impinger. Set up the train without the probe as in Figure 5-1. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 in. Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250° F. at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70° F. or less. Temperatures above 70° F. may result in damage to the dry gas meter from either moisture condensation or excessive heat.

4.1.3 Particulate train operation. For each run, record the data required on the example sheet shown in Figure 5-2. Take readings at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in section 4.2.

[1] Trade name.

[1] Trade name.

[2] Dry using Drierite[1] at 70° F. ± 10° F.

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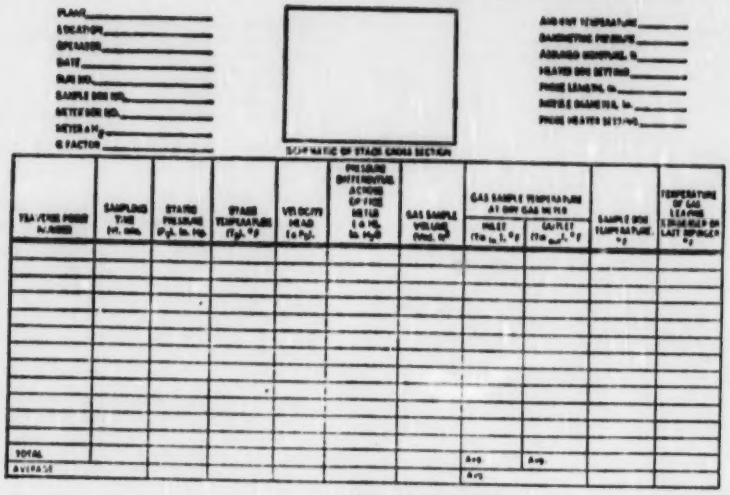


Figure 5-2. Particulate field data.

4.2 Sample recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers, then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to lose adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

4.3 Analysis. Record the data required on the example sheet shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2. Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. *Calibration.*

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. *Calculations.*

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-3).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F., 29.92 inches Hg) by using Equation 5-1.

$$V_{m_{std}} = V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71\ \frac{^\circ R}{in.\ Hg}\right)V_m\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{T_m}\right)$$

equation 5-1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of water vapor.

$$V_{w_{std}} = V_{l_c}\left(\frac{\rho H_2O}{M H_2O}\right)\left(\frac{RT_{std}}{P_{std}}\right) = \left(0.0474\ \frac{cu.\ ft.}{ml.}\right)V_{l_c}$$

equation 5-2

where:

$V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cu. ft.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

ρH_2O = Density of water, 1 g./ml.

MH_2O = Molecular weight of water, 18 lb/lb.-mole.

R = Ideal gas constant, 21.83 inches Hg—cu. ft./lb.-mole-°R.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.4 Moisture content.

$$B_{ws} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}}$$

equation 5-3

where:

B_{ws} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cu. ft.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total particulate weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure 5-3).

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154\ \frac{gr.}{mg.}\right)\left(\frac{M_n}{V_{m_{std}}}\right)$$

equation 5-4

where:

c'_s = Concentration of particulate matter in stack gas, gr./s.c.f., dry basis.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

PLANT_____

DATE_____

RUN NO._____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER. (1 g/ml):

$$\frac{\text{INCREASE, g}}{\text{(1 g/ml)}} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

6.6.2 Concentration in lb./cu. ft.

$$c_s = \frac{\left(\frac{1}{453{,}600}\ \frac{\text{lb.}}{\text{mg.}}\right)M_n}{V_{m(std)}} = 2.205\times10^{-6}\frac{M_n}{V_{m(std)}} \qquad \text{equation 5-5}$$

where:

c_s = Concentration of particulate matter in stack gas, lb./s.c.f., dry basis.

453,600 = Mg/lb.

M_n = Total amount of particulate matter collected, mg.

$V_{m(std)}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.7 Isokinetic variation.

$$I = \frac{T_s\left[\frac{V_{lc}(\rho_{H_2O})R}{M_{H_2O}} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n \left(1.667\ \frac{\text{min.}}{\text{sec.}}\right)} \times 100$$

$$= \frac{T_s\left[\left(0.00267\ \frac{\text{in. Hg-cu. ft.}}{\text{ml.-°R}}\right)V_{lc} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \qquad \text{Equation 5-6}$$

where:

I = Percent of isokinetic sampling.

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Fig. 5-3), ml.

ρ_{H_2O} = Density of water, 1 g/ml.

R = Ideal gas constant, 21.83 inches Hg-cu. ft./lb.-mole-°R.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °R.

P_{bar} = Barometric pressure at sampling site, inches Hg.

ΔH = Average pressure drop across the orifice (see Fig. 5-2), inches H_2O.

T_s = Absolute average stack gas temperature (see Fig. 5-2), °R.

θ = Total sampling time, min.

V_s = Stack gas velocity calculated by Method 2, Equation 2-2, ft./sec.

P_s = Absolute stack gas pressure, inches Hg.

A_n = Cross sectional area of nozzle, sq. ft.

6.8 Acceptable results. The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 110\%$, the results are acceptable, otherwise, reject the results and repeat the test.

7. *Reference.*

Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

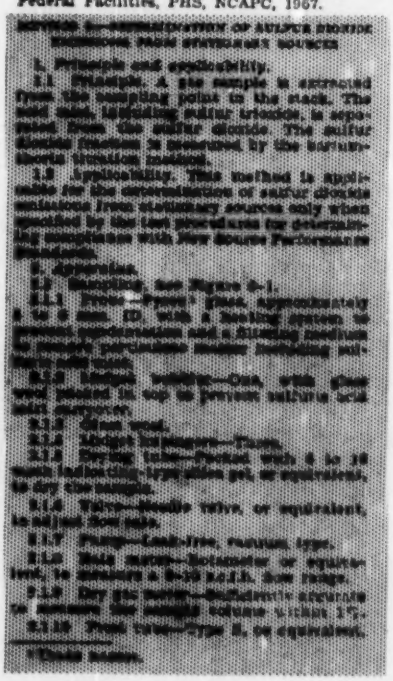
Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581.

Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0576.

Smith, W. S., R. T. Shigehara, and W. F. Todd, A Method of Interpreting Stack Sampling Data, Paper presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment, APCA paper No. 67-119, 1967.

Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.



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APPENDIX B

STATISTICAL METHODS

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APPENDIX B. STATISTICAL METHODS

This appendix is composed of various independent sections, each of which contains a statistical analysis pertinent to a particular question or problem encountered in the analysis of the Method 5 collaborative test data. Reference to these sections has been made at various junctures in the Statistical Design and Analysis part of the main report.

B.1 Preliminary Data Analysis

An initial scan of the original particulate concentrations reported by the four collaborators and shown in Table 2 of the main report disclosed consistently high values from Lab 103. No calculation errors could be located to account for this discrepancy. As discussed in Section III.C of the main report, it was discovered during a subsequent visit that Lab 103 had included extracted condensibles with its probe particulate catch to obtain its total collected particulate matter. Consequently, Lab 103 had to be excluded from the entire data analysis.

An outlier analysis was performed on the original particulate data reported by the three remaining collaborators. When any of the three collaborators' values for a run differed by more than 10 percent from either of the other two, the Method 5 particulate matter calculation of the outlying value was rechecked. During this process, some calculation errors and frequent deficient round-off procedures were discovered. Since the calculation deficiencies were so prevalent, all the calculations pertinent to Method 5 were recomputed from the raw data for each collaborator on every run. These pertinent calculations include the corrected gas volume $V_{m_{std}}$, the particulate matter concentration c, and the percent of isokinetic sampling I. The recalculated values for c, I, and $V_{m_{std}}$ are displayed in Table 3 in the main report.

Even a cursory comparison of Table 3 against Table 2 reveals that calculation is a major source of error in Method 5. Hence, an examination of where mistakes and excessive intermediate round-off commonly occurred in the calculations is appropriate. Lab 101 consistently misused the stack gas temperature $(T_s)_{avg}$ and velocity head $(\sqrt{\Delta p})_{avg}$ from the preliminary traverse for setting the nomograph rather than from the actual run sampling in computing the stack gas velocity $(V_s)_{avg}$ and the percent of isokinetic sampling I. Lab 102 calculated the stack gas pressure P_s incorrectly, correcting the barometric pressure by the tabulated orifice meter average instead of using the tabulated static pressure average; since no formula is presented in the "Standards of Performance for New Stationary Sources" for computing P_s, this or some similar P_s calculation error could frequently occur. Lab 104 was inconsistent in the application of its dry gas meter volume correction factor. All three laboratories were somewhat remiss in rounding intermediate calculations, but Lab 101 often rounded the ratio $M_n/V_{m_{std}}$ of particulate mass to gas sampled to one significant digit; never did it retain more than two significant digits in this critical factor of the particulate concentration calculation equation 5-5 (cf. Appendix A). In computing $V_{m_{std}}$, Lab 101 always truncated the dry gas meter volume-to-temperature ratio (V_m/T_m) to two digits before inserting this factor in the $V_{m_{std}}$ calculation equation. In computing the velocity head $(\sqrt{\Delta p})_{avg}$, Labs 101 and 104 only summed the two most significant digits from the square roots of the Δp readings; this frequently introduced errors of 1- to 2-percent in the velocity head calculation, which were carried directly in the $(V_s)_{avg}$ and I calculations. Lab 101 only carried its calculation of the nozzle area A_n to one significant digit, thereby introducing a 14 percent positive error into its calculation of I.

B.2 The High Particulate Concentration Determination Phenomenon

Table 3 contains four extremely high particulate concentration determinations, all of which were obtained by Lab 101, on Runs 4, 9, 10, and 13. Since no violation of Method 5 procedures could be ascertained, these must be considered valid Method 5 determinations. However, because they are bound to cause the majority of the Method 5 precision variability reported for this collaborative test, it is important to find out why they occurred.

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This high particulate concentration phenomenon has occurred in all three of the Method 5 collaborative tests that have been conducted. In addition to the four high values in this cement plant test, six high values were obtained by the three included laboratories in the Allen King Power Plant collaborative test[7], and two high values occurred in the Holmes Road incinerator collaborative test[8]. An examination of these 12 high determinations revealed that, in 11 of the 12 cases, the reason for the high particulate concentration was an extraordinary amount of particulate matter present in the acetone washings. The pertinent data are shown in Table B-1. The only high sample that had a normal particulate content in its acetone wash was Run 3 by Lab 104 in the incinerator plant test.

Table B-1. Examination of High Particulate Concentrations from All Three Collaborative Tests of Method 5

Site	Lab	Run	Particulate Matter					
			Conc. 10^{-7} lb/scf	Mass, mg.				
				Total	Acetone Wash	Normal Acetone Wash Range for Lab	Median for Lab	Excessive Acetone Wash
Cement Plant	101	4	137.0	387.4	374.1	12 to 50	35	340
	101	9	148.8	394.4	381.1	12 to 50	35	345
	101	10	137.4	383.3	371.0	12 to 50	35	335
	101	13	214.2	609.2	510.0	12 to 50	35	475
Power Plant	102	7	335.7	1065.7	581.3	200 to 450	250	330
	102	9	405.3	1270.5	788.7	200 to 450	250	540
	103	7	313.9	1036.8	490.6	80 to 420	180	310
	104	1	334.4	878.3	542.9	80 to 270	150	390
	104	3	375.1	1349.9	1012.2	80 to 270	150	860
	104	11	351.2	1188.4	611.2	80 to 270	150	460
Incinerator	101	8	469.0	1288.0	675.0	30 to 225	60	615
	104	3	374.6	1050.0	30.5	10 to 100	40	−10

On all the other 11 high determination samples, which we will term the high acetone wash samples, the laboratory found much more particulate matter in these acetone washings than in the acetone washings of any of the normal concentration range samples it obtained in the test. The excessive amount of particulate matter in the acetone washings of these samples over the laboratory median is listed in the last column of Table B-1. For the 11 high acetone wash samples, the excessive particulate matter in the acetone wash ranges from 310 mg to 860 mg, with a median of 390 mg.

In our opinion, the cause of the excessive amount of particulate matter in the acetone wash of these 11 samples is the scraping of particulate matter from the stack wall into the probe tip during the insertion or removal of the sampling train from a sampling port. This scraping hypothesis explains all the observed features of the high value phenomenon. If the probe tip did scrape up particulate matter as the sampling train was being inserted or removed, this excessive particulate matter would be washed from the probe during sample recovery and would consequently appear in the acetone washings. Scraping of the probe tipe against the stack wall would only occur occasionally; therefore, our hypothesis does account for both the discrete nature (either obviously present or entirely absent) and the infrequent occurrence of the high value phenomenon. Since the likelihood of contaminating the probe tip by scraping would vary with the dirtiness of the stack inner wall and with the carefulness of the sampling team, the scraping hypothesis does explain the observed variation in high value frequency from one site to another and from one laboratory team to another. Finally, brushing the probe tip against the stack wall would scrape a considerable amount of particulate matter into the tip; the scraped amount could well equal the observed excessive amount which ranged from 310 mg to 860 mg. Thus, the scraping hypothesis is the probable explanation for the high particulate concentration determinations that inflate the precision of Method 5.

B.3 Examination of the Final Port Effect

Each collaborative team was supposed to sample isokinetically for 30 min from each of the four ports in taking a Method 5 sample; therefore, one would not expect a port effect with Method 5. However, it is believed that on some samples, the probe tip was accidently scraped against the inner stack wall during insertion or removal of the probe, thereby contaminating the tip with excessive particulate matter. Because there is a possibility of a port effect in this collaborative test, the question was subjected to a statistical test.

Youden's Rank Test[9] is used to determine whether there was any significant detectable final port effect. The test for final port effect is presented in Table B-2. Each port is assigned a rank on each run based on the particulate matter concentration determined for the sample having that port as its final sampling port. The final ports corresponding to all rejected samples (Lab 103 determinations, missing values, or unacceptable isokinetic sampling at $80 \leq I \leq 120$) are assigned median ranks of 2.50. The other final ports are then assigned the ranks 1.25, 2.50, and 3.75, according to the corresponding concentration determinations. The port ranks are summed over all 15 runs to give the final port rank score.

Table B-2. Youden Rank Test for Significance of Final Port Effect

Run	Ranked Data by Final Port Sampled			
	Port A	Port B	Port C	Port D
1	1.25	2.50	3.75	2.50
2	1.25	3.75	2.50	2.50
3	1.25	3.75	2.50	2.50
4	1.25	2.50	3.75	2.50
5	2.50	3.75	2.50	1.25
6	2.50	3.75	2.50	1.25
7	2.50	1.25	2.50	3.75
8	3.75	2.50	1.25	2.50
9	3.75	2.50	2.50	1.25
10	2.50	3.75	2.50	1.25
11	2.50	2.50	1.25	3.75
12	2.50	3.75	2.50	1.25
13	3.75	2.50	2.50	1.25
14	2.50	3.75	2.50	1.25
15	1.25	2.50	3.75	2.50
Final Port Rank Scores:	35.00	45.00	38.75	31.25
Null Hypothesis:	The true particulate concentration sampled is equivalent, regardless of the final port sampled.			
Alternative Hypothesis:	The particulate concentration sampled differs systematically, depending on the final port sampled.			
Approximate 5 Percent Two-Tailed Limits:	(28.1, 46.9)			
Conclusion:	Because there are no final port scores outside the 5 percent limits, the alternative hypothesis is rejected in favor of the null hypothesis. There is no significant final port effect.			

The null hypothesis to be tested is that there is no final port effect, i.e., that the true particulate concentration sampled is equivalent, regardless of the final port used. This hypothesis should be rejected in favor of the alternative that there is a systematic final port effect, at the 0.05 significance level, if any of the final port rank scores fall outside the two-tailed limits of 28.1 and 46.9. Since all the final port rank scores (35.00, 45.00, 38.75, and 31.25) are between 28.1 and 46.9, the null hypothesis should not be rejected. Thus, any significant final port effect is not detectable.

B.4 Grouping the Samples into Blocks

Even with the high values eliminated, Table 3 shows tremendous variation in the Method 5 particulate concentration determinations from one run to another. It is reasonable to assume that Method 5 concentration determinations for various runs reflect the ordering of the true particulate concentrations in the stack while those runs were taken. With this assumption, the Kruskal-Wallis *H* Test[10] can be applied to the acceptable Method 5 concentration determinations for the 15 runs to determine whether the true particulate concentration did indeed vary from run to run. This *H* Test is summarized in Table B-3. Acceptable Method 5 concentration determinations for this test are those sampled isokinetically ($90 \leq I \leq 110$) and not high values.

Table B-3. Kruskal-Wallis H Test for Differences in the True Particulate Concentration from Run to Run

Run	Acceptable Method 5 Particulate Conc. Determinations,* 10^{-7} lb/scf	Ranks of Determinations	Number Accept. Determ., n_i	Rank Sum, R_i
1	12.9, 13.0, 16.0	11, 12.5, 17	3	40.5
2	13.1, 14.5	12.5, 14	2	26.5
3	10.3, 10.9, 12.4	5, 8, 10	3	23
4	18.8	18	1	18
5	10.8	7	1	7
6	8.6, 10.5	2, 6	2	8
7	9.4	4	1	4
8	15.5, 15.9, 29.2	15, 16, 24	3	55
9	6.8, 9.0	1, 3	2	4
10	12.3	9	1	9
11	20.7, 28.7	20, 23	2	43
12	33.4, 38.9	25, 26	2	51
13	52.3, 75.3	27, 28	2	55
14	19.8	19	1	19
15	26.9, 27.0	21, 22	2	43
			$N = 28$	

Null Hypothesis:	The true particulate matter concentration of every run is the same.
Alternative Hypothesis:	The true particulate matter concentration differs from one run to another.
H Test Statistic:	$H = \frac{12}{N(N+1)} \sum_{i=1}^{15} \left(\frac{R_i^2}{n_i}\right) - 3(N+1) = \frac{12}{812}(7615.5) - 3(29) = 25.54$
Approximate 5 Percent and 2.5 Percent Limits:	$\chi^2_{0.95}(14) = 23.7$ $\chi^2_{0.975} = 26.1$
Conclusion:	Since $H = 25.54 > \chi^2_{0.95}(14) = 23.7$, the null hypothesis is rejected at the 0.05 significance level. The true particulate matter concentration does differ from one run to another.

*Acceptable under the isokinetic restriction $90 \leq I \leq 110$; high values eliminated.

Each acceptable determination is assigned a rank in ascending concentration order. Rank sum R_i is computed for run i as the sum of its n_i ranks. With a total of $N = 28$ ranks assigned, the H Test statistic is

$$H = \frac{12}{N(N+1)} \sum_{i=1}^{15} \left(\frac{R_i^2}{n_i}\right) - 3(N+1) = 25.54$$

It tests the null hypothesis of identical true particulate matter concentrations on every run; a high H statistic rejects this null hypothesis. Since $H = 25.54$ exceeds the 5 percent limit $\chi^2_{.95}(14) = 23.7$, the null hypothesis is rejected at the 0.05 significance level. The true particulate matter concentration did differ from one run to another. Grouping the runs into blocks having approximately the same true particulate concentration is the first-order statistical technique for coping with this true variation problem.

The approximate ordering of the true particulate matter concentrations for the 15 runs can be estimated from the appropriate cement plant operating conditions. Data on two operating variables, the daily feedrate and the stack opacity, are available. The daily feedrate is calculated from the tons of dry feed materials input to the cement plant each day and from the number of kilns (two or three) in use that day. Since the daily feedrate is a 24-hour average, it provides little direct information about the true particulate concentration in the stack during the 2 hours in which a run was made. The opacity of the stack plume being tested was measured by an in-plant bolometer on a strip chart recorder. Both the peak opacity recorded during the sample's collection and the time-weighted average opacity over the sampling period are useful measures of the true particulate concentration. The daily feedrates, the time-weighted average opacity, and peak opacity for each run are listed in Table B-4. Each run is assigned a feed rank R_f, an average opacity rank R_a, and a peak opacity rank R_p based on the values of the corresponding operating condition variables. A rank score is computed for each run from the

Table B-4. Run Particulate Concentration Ranks from Cement Plant Operating Conditions

Run	Date	Daily Feed Rate		Opacity from Transmissometer				Rank Score, $R_f + R_a + 2R_p$
		Tons Dry Feed per Kiln	Rank, R_f	Time Wtd. Average		Peak Opacity		
				Average, %	Rank, R_a	Peak, %	Rank, R_p	
1	4-2	481.7	1	9.5	3	26	8	20.0
2	4-3	511.3	2	10.5	6.5	29	9	26.5
3	4-4	533.5	4	10.0	5	12	1.5	12.0
4	4-5	573.1	7.5	14.0	12.5	20	6	32.0
5	4-5	573.1	7.5	10.7	8	16	4	23.5
6	4-6	517.0	3	9.0	1	42	11	26.0
7	4-9	604.9	12.5	10.5	6.5	16	4	27.0
8	4-9	604.9	12.5	13.0	9.5	66	12	46.0
9	4-10	548.1	5.5	9.5	3	12	1.5	11.5
10	4-10	548.1	5.5	13.0	9.5	16	4	23.0
11	4-11	603.6	10.5	9.5	3	39	10	33.5
12	4-11	603.6	10.5	14.0	12.5	69	13	49.0
13	4-12	609.4	14.5	15.5	15	79	14	57.5
14	4-12	609.4	14.5	14.5	14	21	7	42.5
15	4-13	602.4	9	13.3	11	88	15	50.0

formula, rank score = $R_f + R_a + 2R_p$. The peak opacity rank R_p receives a double weight because it is believed to be the best particulate concentration indicator. The ranks and rank scores for each run are also presented in Table B-4. The ordering of the runs that is produced by the rank score is shown in Table B-5. Our assumption is that the rank score provides an objective criterion for ordering the runs according to their true particulate concentration. Since the correlation between the rank score in the first column of Table B-5 and the collaborators' Method 5 mean in the last column of Table B-5 is $r = 0.8144$, an extremely significant correlation, this assumption seems justified. Thus, Runs 9 and 3, with rank scores of 11.5 and 12.0, respectively, had the lowest average true particulate concentration, while Run 13 with a 57.5 rank score had the highest true concentration.

The runs are grouped into blocks by their rank scores. Listing the rank scores in ascending order in Table B-5 shows two useful breaks, between 27.0 and 32.0 and between 50.0 and 57.5. These break points divide the runs into the three groups that minimize the within-group mean square variation of the rank score-ordered Method 5 run means. Thus these break points are used as the block boundaries. Therefore, as TableB-5 shows, Block 1 consists of Runs 9, 3, 1, 10, 5, 6, 2, and 7. Runs 4, 11, 14, 8, 12, and 15 comprise Block 2. Run 13 is in a block by itself, Block 3.

Table B-5. Blocking the Runs by Rank Score

Rank Score	Run	Block	Collaborators' Method 5 Mean with High Values Eliminated	
			$80 \leq I \leq 120$	$90 \leq I \leq 110$
11.5	9	1	7.9	7.9
12.0	3	1	11.2	11.2
20.0	1	1	14.0	14.0
23.0	10	1	9.3	12.3
23.5	5	1	10.8	10.8
26.0	6	1	9.0	9.6
26.5	2	1	13.1	13.8
27.0	7	1	13.9	9.4
32.0	4	2	15.3	18.8
33.5	11	2	21.7	24.7
42.5	14	2	14.7	19.8
46.0	8	2	20.2	20.2
49.0	12	2	31.2	36.2
50.0	15	2	24.3	27.0
57.5	13	3	63.8	63.8

B.5 Data Adjustment for True Concentration Variation Within Block

It is demonstrated in Section B.6 that the proportionality of standard deviation to mean is characteristic of Method 5 data. The between-laboratory proportionality $\sigma_b = \beta_b\delta$ is derived from analysis of the Method 5 run results, while the within-laboratory proportionality $\sigma = \beta\delta$ emerges from a study of collaborator block results. By definition of the laboratory bias standard deviation $\sigma_L = \beta_L\delta$ where $\beta_L = \sqrt{\beta_b^2 - \beta^2}$. Thus the coefficient of variation is a legitimate device for expressing the Method 5 variation.

In the Method 6 collaborative test report,[11] it was shown that the within-to-between coefficient of variation ratio $\hat{\beta}/\hat{\beta}_b$ should usually lie between 0.3 and 0.95. Values of $\hat{\beta}/\hat{\beta}_b \geq 1.0$ result in a zero laboratory bias standard deviation estimate, $\hat{\sigma}_L = o$, implying that all laboratories obtain equivalent Method 5 concentration determinations.

The values of the $\hat{\beta}/\hat{\beta}_b$ ratio for Blocks 1 and 2 of the Method 5 collaborative test data, accepted under the isokinetic restriction ($90 \leq I \leq 110$), are shown in Table B-6. There is no Block 3 estimate because with only one run in Block 3, no estimation of within-laboratory variation is possible. Both ratios, 1.40 for Block 1 and 1.10 for Block 2, considerably exceed 1.0. While these ratios do occasionally exceed 1.0 by chance, there are sufficient degrees of freedom in the $\hat{\beta}$ and $\hat{\beta}_b$ estimates to conclude that there is a reason why they both exceed 1.0. There are two possibilities: either there actually are no differences between laboratories in their performance of Method 5, or the true particulate concentrations of the runs grouped in a block were substantially different.

Table B-6. Block Coefficient of Variation Ratios

Block	Block Coefficient of Variation Estimate*		
	Between Labs, $\hat{\beta}_b$	Within Labs, $\hat{\beta}$	Ratio, $\hat{\beta}/\hat{\beta}_b$
1	0.1524	0.2133	1.40
2	0.2152	0.2370	1.10
3	0.3211	–	–

*Only data acceptable under the isokinetic restriction $90 \leq I \leq 110$ are included. The four high values are excluded from the data.

The first possibility, that there are no true differences between laboratories, can be verified by Youden's Rank Test. The test is presented in Table B-7. Each laboratory is assigned a rank on each run in the order of its particulate concentration determination. The number of 1 is assigned to the lowest determination, 2 to the middle (or rejected) determination, and 3 to the highest determination. The three runs with none or only one acceptable determination, Runs 5, 7, and 14, are not ranked. The null hypothesis is that there is no laboratory effect, i.e., that all laboratories perform Method 5 in an equivalent manner. This hypothesis should be rejected at the 0.05 significance level if any lab rank score is outside the two-tailed limits of 18.1 and 29.9. Since both the Lab 101 rank score of 34 and the Lab 102 rank score of 16 are outside these limits, the null hypothesis must be rejected. Method 5 determinations do possess a laboratory effect which produces systematic differences between laboratories. Therefore, σ_L for Method 5 is significantly larger than zero. The first possible explanation is rejected. Thus, we conclude that there were substantial differences in true particulate matter concentration, even on the runs which have been grouped in the same block.

Table B-7. Youden Rank Test for Significance of Laboratory Effect

Run	Ranked Data*		
	Lab 101	Lab 102	Lab 104
9	3	1	2
3	3	1	2
1	3	1	2
10	3	1	2
5	–	–	–
6	3	1	2
2	3	1	2
7	–	–	–
4	3	1	2
11	3	1	2
14	–	–	–
8	3	2	1
12	1	3	2
15	3	1	2
13	3	2	1
Lab Rank Scores:	34	16	22
Null Hypothesis:	All laboratories perform Method 5 in an equivalent manner.		
Alternative Hypothesis:	Method 5 determinations differ systematically from laboratory to laboratory.		
Approximate 5 Percent Two-Tailed Limits:	(18.1, 29.9)		
Conclusion:	Since the Lab 101 and Lab 102 rank scores both lie outside the two-tailed limits, one must reject the null hypothesis in favor of its alternative. Method 5 possesses a laboratory effect which produces systematic differences in the Method 5 determinations of different laboratories.		

*Only data acceptable under the isokinetic restriction $90 \leq I \leq 110$ are included.

Because the true particulate concentration did differ substantially, even on the runs in the same block, the within-laboratory standard deviation estimates obtained from a straightforward coefficient of variation analysis of the acceptable Table 3 data will be grossly inflated. Thus to obtain more realistic within-laboratory estimates, the data need to be adjusted for the true concentration before making these estimates. However, the true particulate matter concentration existing in the stack during a run is unknown. No valid particulate concentration monitor took simultaneous readings during the runs. Even the approximating total rank score developed in Section B.4 and presented in Table B-5 is too crude for this purpose—it is essentially an ordering rather than a measuring variable. The only valid indicator of the true particulate matter concentration during a run is the collaborators' Method 5 run mean. With the high value samples eliminated, these run means are listed in Table B-5 for both the $80 \leq I \leq 120$ and the $90 \leq I \leq 110$ isokinetic acceptance ranges. We will assume that the differences between these run means, for the runs in a block, are equal to the differences in the true concentrations for these runs. A workable data adjustment technique for obtaining realistic, albeit somewhat conservative, within-laboratory estimates results from this assumption. Each collaborator's determination on a run is adjusted by the amount necessary to give the run the same mean as its block. So, every run in a block of adjusted data has the same run mean. The data adjustment formula used is

$$y_{ij} = x_{ij} + (\bar{x}_{.j} - \bar{x}_{..})$$

where x_{ij} is the corrected concentration determination reported in Table 3 for collaborator i on run j, $\bar{x}_{.j}$ is the run j mean, and $\bar{x}_{..}$ is the block mean. This adjustment formula is applied to the Block 1 and Block 2 determinations in the acceptable $90 \leq I \leq 110$ isokinetic range, with the high values eliminated. The resulting adjusted data are presented along with its run summary in Table B-8. The corresponding collaborator block summary is shown in Table 6 of the main report. In Table B.8, the symbol E follows an eliminated high value, M denotes a missing determination, and R identifies an isokinetically rejected sample. The $\hat{\beta}/\hat{\beta}_b$ ratios of Blocks 1 and 2 are reduced from 1.40 and 1.10 for the corrected data to 0.44 and 0.76 for the adjusted data. So the $\hat{\beta}/\hat{\beta}_b$ ratios for the adjusted data are in the usual range. Although the adjustment technique is probably too severe, the adjusted data provide a more suitable basis on which to perform the within-laboratory precision analysis.

Table B-8. The Adjusted Method 5 Data and Its Run Summary

Run	Acceptable Method 5 Particulate Concentration Determinations with High Values Excluded, 10^{-7} lb/scf			Run Summary		
	Lab 101	Lab 102	Lab 104	Mean, $\bar{x}_j$	Standard Deviation, s_j	Coef. of Variation, $\hat{a}_j$
9	E	10.0	12.2	11.10	1.56	0.1756
3	12.3	10.2	10.8	11.10	1.08	0.1100
1	13.2	10.0	10.2	11.13	1.79	0.1817
10	E	11.1	R	11.10		
5	11.1	M	R	11.10		
6	12.1	10.2	R	11.15	1.34	0.1510
2	11.8	10.4	R	11.10	0.99	0.1118
7	R	R	11.1	11.10		
4	E	24.4	R	24.40		
11	28.4	20.4	R	24.40	5.66	0.2906
14	M	24.4	R	24.40		
8	33.4	20.1	19.7	24.40	7.80	0.3606
12	21.7	27.2	R	24.45	3.89	0.1994
15	24.5	24.4	R	24.45	0.07	0.0036
13	E	75.3	52.2	63.75	16.33	0.3211

Note:
E–Excluded determination: high concentration probably caused by scraping probe tip against stack wall.
M–Missing determination.
R–Rejected determination: outside acceptable isokinetic sampling range, $90 \leq I \leq 110$.

B.6 Relationship of the Standard Deviation to the Mean

The coefficient of variation approach is an ideal procedure for estimating the precision of a test method from collaborative test data, both because it yields percentage precision estimates which the non-statistician can quickly comprehend, and because estimates of the basic between-laboratory and within-laboratory standard deviations derive naturally from it. Application of the coefficient of variation procedure requires justification of its fundamental assumption, namely, that the precision standard deviations of the method's determinations are actually proportional to their mean value. The precision standard deviations for which the proportional relationship needs to be verified are the between-laboratory standard deviation for run results and the within-laboratory standard deviation for collaborator block results. This section presents the necessary verification information for Method 5 from the corrected cement plant collaborative test data.

The direct evidence for proportionality comes from plotting and regressing the pertinent standard deviation versus mean data. The values of the between-laboratory standard deviations and means for each run are presented in the run summaries of Tables 4 and 5 in the main report. Table 4 includes the four high values, along with all the $90 \leq I \leq 110$ isokinetically acceptable particulate concentration determinations. Table 5 excludes these values, but retains the $90 \leq I \leq 110$ isokinetic sampling limitation. The run standard deviation and mean results from Table 4 are plotted in Figure B-1. These data do not exhibit a very proportional relationship because the four high value runs, having standard deviations between 80 and 90×10^{-7} lb/scf, are so distinct from the other runs. Removing the high concentration determinations from these four runs yields the corresponding Table 5 results which are plotted in Figure B-2. A straight line passing through the origin provides a good fit of the Figure B-2 points; this suggests a valid proportional relationship. A qualitative assessment of the

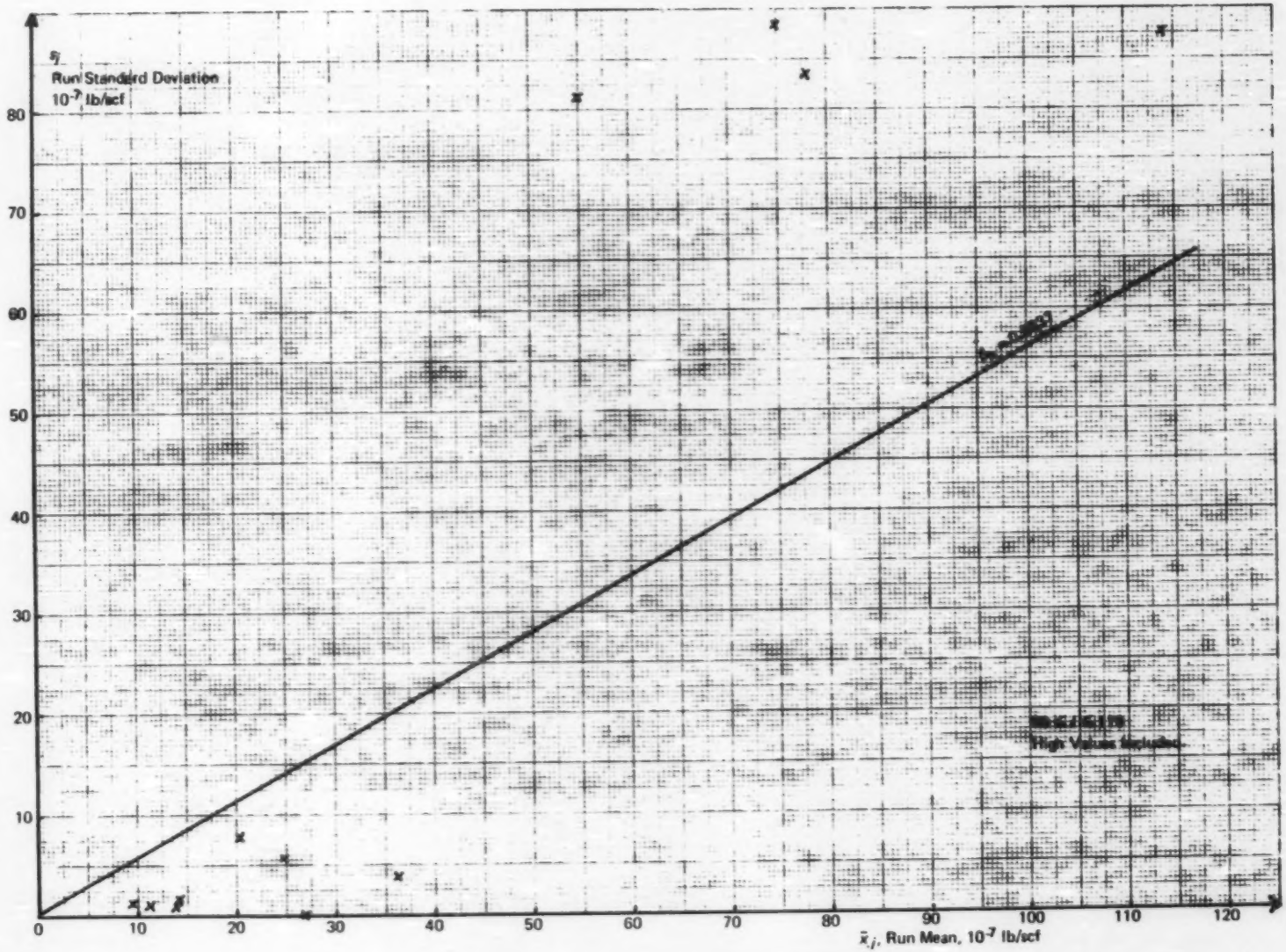

Figure B-1. Between-Laboratory Run Plot

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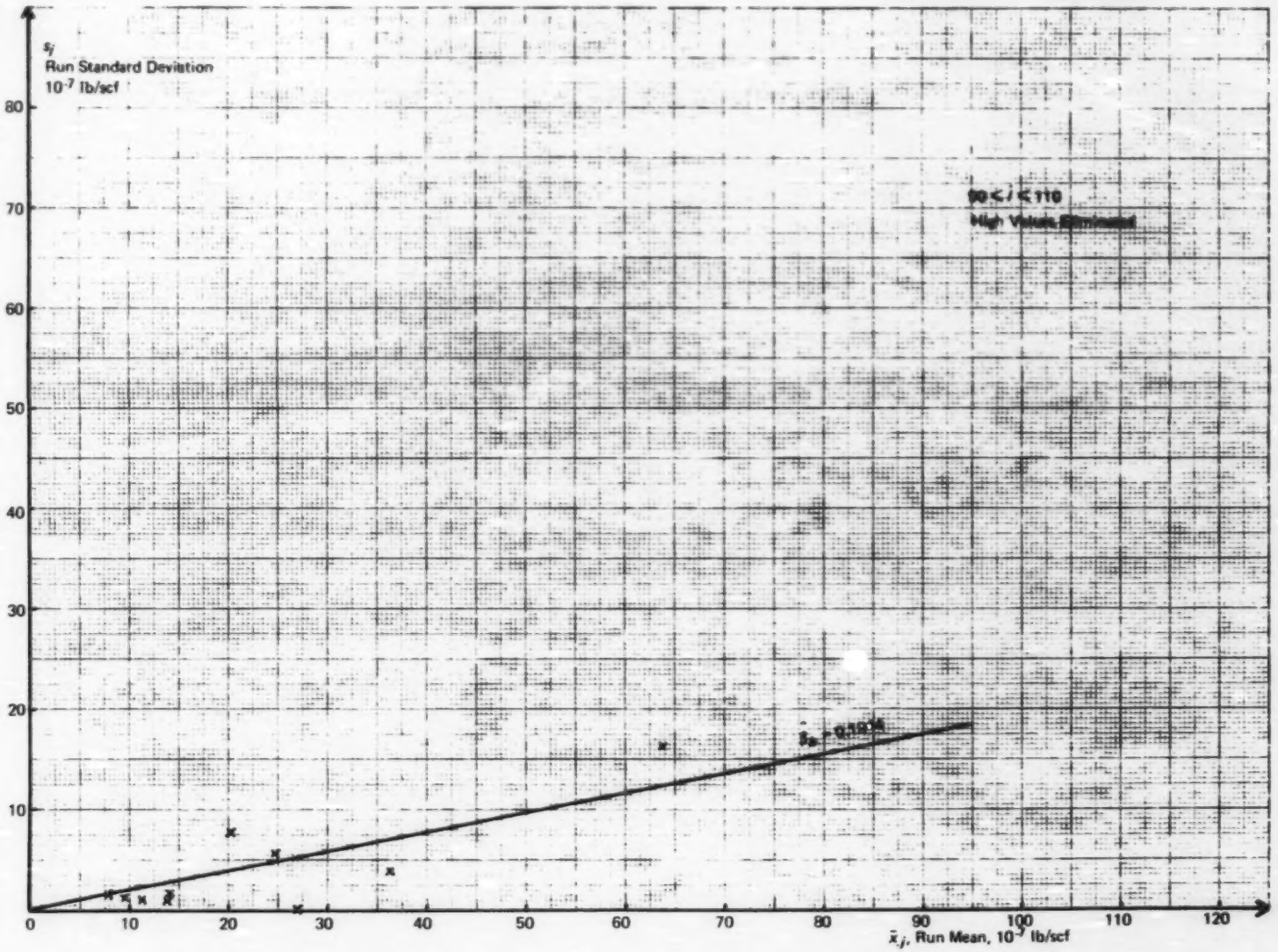

Figure B-2. Between-Laboratory Run Plot Excluding High Values

proportionality of run standard deviation to mean is obtained by comparative regression of the run standard deviation against various functions of the mean. The functions of the mean $\bar{x}$, that are regressed through the origin against the standard deviation s, as $\hat{s} = af(\bar{x})$, are $\bar{x}^{-1}$, $\bar{x}^{1/4}$, $\bar{x}^{1/2}$, $\bar{x}^{3/4}$, $\bar{x}$, $\bar{x}^{5/4}$, $\bar{x}^{3/2}$, $\bar{x}^{2}$, and $\log \bar{x}$. A summary of the regression results obtained is presented in Table B-9. For the Table 4 run results (high values included, and a $90 \leq I \leq 110$ isokinetic sampling restriction), the regression of $\bar{x}^{5/4}$ against s gives the best correlation, $r_B = 0.9338$, but the proportional

Table B-9. Proportionality Evidence from Comparative Regressions

Type of Std. Dev., s, vs. Mean, $\bar{x}$, Results Regressed	Data Base			Regression Summary*			
	Source Table	Use of High Values	Isokinetic Sampling Restriction	Best Single Variable Regression through Origin		Mean Regression through Origin	
				Best Variable	Correlation Coef., r_B	Equation Coef., a	Correlation Coef., $r_{\bar{x}}$
Run	4	Included	$90 \leq I \leq 110$	$\bar{x}^{5/4}$	0.9338	0.8969	0.9283
	5	Excluded	$90 \leq I \leq 110$	$\bar{x}^{3/2}$	0.9241	0.2000	0.9001
		Excluded	$80 \leq I \leq 120$	$\bar{x}$	0.9594	0.2623	0.9594
Collaborator Block (Adjusted Data)	6	Excluded	$90 \leq I \leq 110$	$\bar{x}^{2}$	0.9874	0.1351	0.9346
		Excluded	$80 \leq I \leq 120$	$\bar{x}$	0.9759	0.1446	0.9759

*The functions of the mean $\bar{x}$ regressed against the standard deviation s as $\hat{s} = af(\bar{x})$ are $\bar{x}^{-1}$, $\bar{x}^{1/4}$, $\bar{x}^{1/2}$, $\bar{x}^{3/4}$, $\bar{x}$, $\bar{x}^{5/4}$, $\bar{x}^{3/2}$, $\bar{x}^{2}$, and $\log \bar{x}$.

relationship $\hat{s} = 0.8969\ \bar{x}$, with a correlation coefficient $r_{\bar{x}} = 0.9283$, is almost as good. For the Table 5 run results, with high values excluded and the $90 \leq I \leq 110$ isokinetic sampling limitation, $\bar{x}^{3/2}$ gives a considerably better correlation to s ($r_B = 0.9241$) than the mean $\bar{x}$ itself ($r_{\bar{x}} = 0.9001$). But when the isokinetic sampling limitation on the Table 5 run results with high values excluded is relaxed to $80 \leq I \leq 120$ allowing the utilization of all concentration determinations, then the mean $\bar{x}$ yields the best regression $\hat{s} = 0.2623\ \bar{x}$ with $r_{\bar{x}} = 0.9594$. When enough concentration data are available, comparative regression also supports the idea that the run standard deviation is proportional to the run mean.

The within-laboratory standard deviations and means for each collaborator block of the adjusted data of Table B-8 are shown in Table 6 in the main report. The four high values are excluded, and all samples collected outside the isokinetic limitation $90 \leq I \leq 110$ are rejected from the Table B-8 data from which the Table 6 results are calculated. The collaborator block standard deviation is regressed against various functions of the collaborator block mean, according to the procedure described in the previous paragraph. As the Table B-9 summary shows, the mean square $\bar{x}^2$ produces a considerably better regression through the origin ($r_B = 0.9874$) than the mean regression ($r_{\bar{x}} = 0.9346$). But again, when the isokinetic restriction is relaxed to $80 \leq I \leq 120$ to permit enough data to support a firm conclusion, the mean regression $\hat{s} = 0.1446\ \bar{x}$, with $r_{\bar{x}} = 0.9759$ as its correlation coefficient, proves best. It thus appears that the collaborator block standard deviation is also proportional to its mean.

Indirect evidence regarding the proper relationship of standard deviation to mean is obtained from Bartlett's Test for equality of variance.[12] This test is used to evaluate the linear (no transformation of x), the logarithmic ($\log_{10} x$), and the square root ($\sqrt{x}$) transformations as procedures for

achieving equality of variance for both the run and collaborator block comparisons of the appropriate data. The Bartlett's Test results are shown in Table B-10. On the run evaluations of both the Table 4 and the Table 5 data, the logarithmic transformation yields better equality of between-laboratory

Table B-10. Adequacy of Alternative Transformations to Achieve Equality of Variance

Type of Comparison	Data Base			Test for Equality of Variance		
	Source Table	Use of High Values	Isokinetic Sampling Restriction	Transformation	Bartlett's Test Result	Significance
Run	4	Included	$90 \leq I \leq 110$	Linear: $y = x$	52.8	$Pr\{\chi^2(11) \geq 52.8\} < 0.0001$
				Log: $y = \log_{1.0} x$	32.8	$Pr\{\chi^2(11) \geq 32.8\} = 0.0006$
				Sqr. root: $y = \sqrt{x}$	40.9	$Pr\{\chi^2(11) \geq 40.9\} < 0.0001$
	5	Excluded	$90 \leq I \leq 110$	Linear: $y = x$	20.9	$Pr\{\chi^2(9) \geq 20.9\} = 0.02$
				Log: $y = \log_{1.0} x$	10.7	$Pr\{\chi^2(9) \geq 10.7\} = 0.30$
				Sqr. root: $y = \sqrt{x}$	14.2	$Pr\{\chi^2(9) \geq 14.2\} = 0.13$
Collaborator Block (Adjusted Date)	6	Excluded	$90 \leq I \leq 110$	Linear: $y = x$	25.4	$Pr\{\chi^2(4) \geq 25.4\} < 0.0001$
				Log: $y = \log_{1.0} x$	9.8	$Pr\{\chi^2(4) \geq 9.8\} = 0.04$
				Sqr. root: $y = \sqrt{x}$	17.0	$Pr\{\chi^2(4) \geq 17.0\} = 0.002$

variance than either the linear or the square root transformations. Because the high values are excluded from the Table 5 data, there is a 30-percent chance that an actual underlying equality of run variance process would have produced data with as much between-laboratory scatter as that exhibited by the logarithmically transformed Table 5 data. The collaborator block transformation evaluation based on the adjusted data summarized in Table 6 shows that the logarithmic transformation is also superior in producing equality of within-laboratory variance. In the first Method 7 collaborative test report[13], it was demonstrated that when the logarithmic transformation of a set of data yields equality of variance (so that the data probably have a lognormal underlying distribution), then the standard deviation is proportional to the mean. Thus, the results of Table B-10 imply that both the run and the collaborator block standard deviations are directly proportional to their respective means.

The preceding evidence enables us to conclude that the proportionality of standard deviation to mean is characteristic of Method 5 concentration determinations at cement plants, both between laboratories ($\sigma_b = \beta_b \delta$) and within a single laboratory ($\sigma = \beta\delta$). The proportional between-laboratory relationship follows from the run results discussed above, while the within-laboratory relationship is inferred from the collaborator block results. Hence, the assumption of proportionality of standard deviation to mean, which is the fundamental prerequisite to use of the coefficient of variation procedure, is justified.

B.7 Weighted Coefficient of Variation Estimation

The usual procedure for estimating the between-laboratory coefficient of variation β_b for a test method from a collaborative test is to average the run coefficient of variation estimates $\hat{\beta}_j$ from each of the K runs with a sample size of more than $n_j = 1$ collaborator's determination:

$$\hat{\beta}_b = \frac{1}{K}\sum_{j=1}^{K} \hat{\beta}_j = \frac{1}{K}\sum_{j=1}^{K} \frac{\alpha_{n(j)} s_j}{\bar{x}_j}$$

Although s_j is a biased estimate of σ_j, the correction factor $\alpha_{n(j)}$ applies the proper adjustment so that $\alpha_{n(j)} s_j$ is unbiased for σ_j and

$$\hat{\beta}_j = \frac{\alpha_{n(j)} s_j}{\bar{x}_j}$$

is unbiased for β when the run j determinations have a normal distribution.

Now intuitively one feels that the run estimates $\hat{\beta}_j$ based on a large sample size n_j, i.e., on simultaneous determinations by a large number of laboratory teams, are better than those based on fewer determinations. With large n_j, the estimate $\hat{\beta}_j$ should have smaller variance. Indeed, this is true.

$$\text{Var}(\hat{\beta}_j) = \text{Var}\left(\frac{\alpha_{n(j)} s_j}{\bar{x}_j}\right)$$

$$= \alpha^2_{n(j)} \text{Var}\left(\frac{s_j}{\bar{x}_j}\right) \qquad \text{since } \alpha_{n(j)} \text{ is a constant on run } j.$$

$$\approx \alpha^2_{n(j)} \left[\frac{\beta_b^2}{2n_j}(1 + 2\beta_b^2)\right] \qquad \text{for normally distributed run } j \text{ determinations (cf. Cramér[14]).}$$

$$\text{Var}(\hat{\beta}_j) = \frac{\alpha^2_{n(j)}}{n_j}\left[\frac{\beta_b^2}{2}(1 + 2\beta_b^2)\right]$$

The variance of $\hat{\beta}_j$ varies with n_j as $[\alpha^2_{n(j)}]/n_j$. Table B-11 enumerates this dependency. There is a drastic reduction in the proportional variance of $\hat{\beta}_j$ as n_j increases.

In this situation, the standard statistical technique for estimating the mean from individual values is to weight each value. Applied to the between-laboratory coefficient of variation, this technique assigns a weight W_j to each run coefficient of variation estimates $\hat{\beta}_j$:

$$\hat{\beta}_b = \frac{1}{K}\sum_{j=1}^{K} W_j \hat{\beta}_j$$

The proper weight to obtain the unbiased between-laboratory coefficient of variation estimate with minimum variance is to set the weight inversely proportional to the variance of $\hat{\beta}_j$ and then standardize the weights so that the average of the W_j is 1.0.[15] This is essentially the same as the procedure recommended for weighting observations in linear least-squares regression.[16] Denote the initial weight for run j as u_j. Then

$$u_j = \frac{1}{\text{Var}(\hat{\beta}_j)} = \frac{n_j}{\alpha^2_{n(j)}}\left[\frac{2}{\beta_b^2(1 + 2\beta_b^2)}\right]$$

The average of the u_j's is

$$\bar{u} = \frac{1}{K}\sum_{i=1}^{K} u_i = \frac{1}{K}\left[\frac{2}{\beta_b^2(1 + 2\beta_b^2)}\right]\sum_{i=1}^{K}\frac{n_i}{\alpha^2_{n(i)}}$$

Table B-11. Sample Size Dependency of Coefficient of Variation Weights

Sample Size, n	Unbiasing Correction Factor α_n	Proportional Variance of Coefficient of Variation Estimate, α_n^2/n	Raw Coefficient of Variation Weight, n/α_n^2
2	1.2533	0.7854	1.273
3	1.1284	0.4244	2.356
4	1.0854	0.2945	3.395
5	1.0638	0.2263	4.418
6	1.0509	0.1841	5.433
7	1.0424	0.1552	6.442
8	1.0362	0.1342	7.451
9	1.0317	0.1183	8.456
10	1.0281	0.1057	9.461
12	1.0230	0.0872	11.466
16	1.0168	0.0646	15.475
20	1.0132	0.0513	19.482
24	1.0109	0.0426	23.485

Then W_j is given by

$$W_j = \frac{u_j}{\bar{u}} = \frac{\dfrac{n_j}{\alpha_{n(j)}^2}\left[\dfrac{2}{\beta_b^2\,(1+2\beta_b^2)}\right]}{\dfrac{1}{K}\left[\dfrac{2}{\beta_b^2\,(1+2\beta_b^2)}\right]\displaystyle\sum_{i=1}^{K}\frac{n_i}{\alpha_{n(i)}^2}}$$

$$W_j = \frac{n_j}{\alpha_{n(j)}^2\left(\dfrac{1}{K}\displaystyle\sum_{i=1}^{K}\dfrac{n_i}{\alpha_{n(i)}^2}\right)}$$

Thus the proper weighted between-laboratory coefficient of variation estimate is

$$\hat{\beta}_b = \frac{1}{K}\sum_{j=1}^{K} W_j\hat{\beta}_j = \frac{1}{K}\sum_{j=1}^{K}\left[\frac{n_j}{\alpha_{n(j)}^2\left(\dfrac{1}{K}\displaystyle\sum_{i=1}^{K}\dfrac{n_i}{\alpha_{n(i)}^2}\right)}\right]\left[\frac{\alpha_{n(j)}s_j}{\bar{x}_j}\right]$$

$$\hat{\beta}_b = \sum_{j=1}^{K}\left[\frac{n_j s_j}{\alpha_{n(j)}\bar{x}_j\displaystyle\sum_{i=1}^{K}\left(\dfrac{n_i}{\alpha_{n(i)}^2}\right)}\right]$$

The same adjustment for differing sample size is also appropriate for the within-laboratory coefficient of variation estimate $\hat{\beta}$. Let us denote the collaborator block index by i and the number of collaborator blocks with more than one determination by L. Then the weighted within-laboratory coefficient of variation estimate is

$$\hat{\beta} = \frac{1}{L}\sum_{i=1}^{L} W_i\hat{\beta}_i = \sum_{i=1}^{L}\left[\frac{n_i s_i}{\alpha_{n(i)}\bar{x}_i \sum_{j=1}^{L}\left(\frac{n_j}{\alpha^2_{n(j)}}\right)}\right]$$

B.8 Precision Standard Deviation Estimation

In this section, the measures of the precision of Method 5 at cement plants are estimated by the weighted coefficient of variation procedure. Two sets of precision measures are calculated, those from all the acceptable collaborative test data shown in Table 4 of the main report, and those from these data with the high values excluded (Table 5 of the main report). The weighted coefficient of variation calculation formulas to be used were derived in the first Method 5 test report[4] and in Section B.7.

The first set of precision measures is applicable to the use of Method 5 as published in the *Federal Register* (cf. Appendix A) at the Portland cement plants. The appropriate source of concentration determination data is Table 4, in which the published isokinetic sampling restriction ($90 \leq I \leq 110$) is imposed; the minimum sampling volume limitation ($V_{m\,std} \geq 60$ scf) is ignored; and the four high value samples are included. The between-laboratory coefficient of variation β_b is estimated from the run point estimates for the 12 runs in Table 4 with more than $n_j = 1$ collaborator's determination. The coefficient of variation point estimate $\hat{\beta}_j$ for run j is weighted by the factor W_j (cf. Table 4) to account for the varying number of collaborators' determinations per run:

$$\hat{\beta}_b = \frac{1}{12}\sum_{j=1}^{12} W_j\hat{\beta}_j = \sum_{j=1}^{12}\left[\frac{n_j s_j}{\alpha_{n(j)}\bar{x}_j \sum_{i=1}^{12}\left(\frac{n_i}{\alpha^2_{n(i)}}\right)}\right] = 0.58368$$

At a true particulate concentration δ, the between-laboratory standard deviation estimate for Method 5 from the cement plant collaborative test is

$$\hat{\sigma}_b = \hat{\beta}_b\,\delta = (0.58368)\delta$$

The usual procedure for estimating the within-laboratory coefficient of variation β is invalidated by the magnitude of the true concentration effect (cf. Sections B.4 and B.5). Adjusted data are needed to eliminate the true concentration effect, but unfortunately the existence of the high values , in the Table 4 data, renders appropriate data adjustment impossible. Our only recourse is to use the within-laboratory and laboratory-bias coefficient of variation estimates, $\hat{\beta}_{(e)}$ and $\hat{\beta}_{L(e)}$ respectively, from the Table 5 and Table 6 data, in which the high values have been eliminated, as a basis for the corresponding Table 4 estimates. Where the subscript e denotes high value elimination, $\hat{\beta}_{(e)}$ and $\hat{\beta}_{L(e)}$ are calculated in the second set of precision measures below. From the nature of high value phenomenon discussed in Section B.2, it is apparent that the high values make a substantial contribution to both the within-laboratory and between-laboratory variability components. Lacking any quantitative information, the safest approach is to apportion the between-laboratory coefficient of variation estimate $\hat{\beta}_b$ between $\hat{\beta}$ and $\hat{\beta}_L$ in the same proportion as $\hat{\beta}_{b(e)} = 0.20123$ is divided into $\hat{\beta}_{(e)} = 0.09788$ and $\hat{\beta}_{L(e)} = 0.17582$. Thus, the within-laboratory coefficient of variation β for the Table 4 data is estimated by proportion:

$$\hat{\beta} = \left(\frac{\hat{\beta}_{(e)}}{\hat{\beta}_{b(e)}}\right)\hat{\beta}_b = \left(\frac{0.09788}{0.20123}\right)(0.58368) = 0.28390$$

The within-laboratory standard deviation estimate is

$$\hat{\sigma} = \hat{\beta}\delta = (0.28390)\delta$$

The laboratory bias coefficient of variation β_L is similarly estimated:

$$\hat{\beta}_L = \left(\frac{\hat{\beta}_{L(e)}}{\beta_{b(e)}}\right)\hat{\beta}_b = \left(\frac{0.17582}{0.20123}\right)(0.58368) = 0.50999$$

Thus $\hat{\sigma}_L = \hat{\beta}_L\,\delta = (0.50999)\delta$ is the estimated laboratory-bias standard deviation. The between-laboratory estimates, based on a maximum of $n_j = 3$ collaborators per run, have $\phi_b = 2$ degrees of freedom. Since the within-laboratory estimates are calculated from the $\hat{\beta}_b$ and $\hat{\beta}_{b(e)}$, each of which possess only 2 degrees of freedom, the within-laboratory estimates also contain just 2 degrees of freedom.

A second set of calculable precision measures would apply to Method 5, at Portland cement plants, if the high value phenomenon could be removed from the method. The proper data are contained in Table 5 along with their run summary; the collaborator block summary of the associated adjusted data is presented in Table 6. Here the isokinetic sampling restriction ($90 \leq I \leq 110$) is still imposed and the minimum sampling volume limitation ($V_{m\,std} \geq 60$ scf) is again ignored, but now the four high value samples are excluded from the acceptable concentration data. The following precision estimates are then obtained:

$$\hat{\beta}_{b(e)} = \frac{1}{10}\sum_{j=1}^{10} W_j\hat{\beta}_j = 0.20123$$

$$\hat{\sigma}_{b(e)} = (0.20123)\delta$$

$$\hat{\beta}_{(e)} = \frac{1}{5}\sum_{i=1}^{5} W_i\hat{\beta}_i = 0.09788$$

$$\hat{\sigma}_{(e)} = (0.09788)\delta$$

$$\hat{\beta}_{L(e)} = \sqrt{(0.20123)^2 - (0.09788)^2} = 0.17582$$

$$\hat{\sigma}_{L(e)} = (0.17582)\delta$$

These between-laboratory estimates again have 2 degrees of freedom. But the within-laboratory values are estimated from the five collaborator blocks and possess a cumulative 20 degrees of freedom. Note that the between-laboratory and within-laboratory standard deviation estimates for Method 5 at cement plants would be reduced to about one-third of their present levels if the high concentration phenomenon could be eliminated.

REFERENCES

1. Environmental Protection Agency, "Standards of Performance for New Stationary Sources," *Federal Register*, Vol. 36, No. 247, December 23, 1971, pp 24876-24890.

2. Dixon, W. J. and Massey, F. J., Jr., **Introduction to Statistical Analysis**, 3rd Ed., McGraw-Hill, New York, 1969, p 136.

3. Environmental Protection Agency, op. cit., p 24880.

4. Hamil, H. F., and Thomas, R. E., "Collaborative Study of Method for the Determination of Particulate Matter Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators)," Southwest Research Institute report for Environmental Protection Agency, June 30, 1974.

5. Hamil, H. F., and Thomas, R. E., "Collaborative Study of Method for the Determination of Particulate Matter Emissions from Stationary Sources (Incinerators)," Southwest Research Institute report for Environmental Protection Agency, July 1, 1974.

6. Youden, W. J., "The Collaborative Test," *Journal of the AOAC*, Vol. 46, No. 1, 1963, pp 55-62.

7. Hamil, H. F., and Thomas, R. E., op. cit., (Fossil Fuel-Fired Steam Generators).

8. Hamil, H. F., and Thomas, R. E., op. cit., (Incinerators).

9. Youden, W. J., op. cit., pp 59-62.

10. Brownlee, K. A., **Statistical Theory and Methodology in Science and Engineering**, 2nd Ed., Wiley, New York, 1965, pp 256-258.

11. Hamil, H. F., and Camann, D. E., "Collaborative Study of Method for the Determination of Sulfur Dioxide Emissions from Stationary Sources (Fossil Fuel Fired Steam Generators,)" Southwest Research Institute report for Environmental Protection Agency, December 10, 1973, pp 35, 36.

12. Brownlee, K. A., op. cit., pp 290-295.

13. Hamil, H. F., and Camann, D. E., "Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel Fired Steam Generators)," Southwest Research Institute report for Environmental Protection Agency, October 5, 1973, pp B-14 to B-16.

14. Cramér, H., **Mathematical Methods of Statistics**, Princeton University Press, Princeton, 1946, p 358.

15. Brownlee, K. A., op. cit., pp 95-97.

16. Draper, N. R., and Smith, H., **Applied Regression Analysis**, Wiley, New York, 1966, pp 77-81.